

SOIL SCIENCE

VOLUME 74

JULY TO DECEMBER, 1952

RUTGERS UNIVERSITY
NEW BRUNSWICK, NEW JERSEY
U. S. A.

PUBLISHED BY
THE WILLIAMS & WILKINS COMPANY
BALTIMORE, MARYLAND

SOIL SCIENCE

Founded 1916 by Jacob G. Lipman

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Entered as second-class matter May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879

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SOIL SCIENCE

VOLUME 74

July 1952

NUMBER 1

SOIL SCIENCE IN THE NETHERLANDS

After the meetings of the Fourth International Congress of Soil Science at Amsterdam during the summer of 1950, visiting scientists were taken on several excursions to study intensity of land use in the Netherlands and problems related thereto. The high population density of that country has required reclamation of land from sea and lake, and the Dutch have pioneered in such enterprises.

With increasing growth in world population, ever-greater emphasis must necessarily be put on food production. Other countries are interested in learning as much as possible about Dutch methods. Accordingly, it was decided to ask the Dutch soil scientists to prepare material for a special issue of SOIL SCIENCE to be devoted exclusively to their techniques and findings.

At our request, a special committee, consisting of P. Bruin, C. H. Edelman, and A. J. Zuur, was appointed to arrange for preparation of the necessary papers. The greater part of this work was done by W. H. van der Molen and W. van der Zweep, under the direction of the committee. We are very much indebted to all these men for their cordial acceptance of this assignment and for the excellent set of papers contained in this issue of the Journal.

FIRMAN E. BEAR

AGRICULTURE

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Any survey of Dutch husbandry would be impossible without considering the relationship of such other economic activities of the country as commerce and industry. It would be impossible, likewise, to deal with the essential problems without considering the density and professional skill of the population.

Individual farmers in many countries try to take advantage of every imaginable opportunity to increase the productivity of their soils, but in the Netherlands this is a common national objective. In consequence, strong moral and economic forces are aroused, and results far exceeding those attainable by individual efforts are being achieved. In this respect, the government exercises a strong influence, for in addition to enforcing statutory provisions, it fosters education, advisory work, and research.

The activities of corporations of farmers and growers in the sphere of agricultural techniques, economics, and organization have shown a marked development of their own. Leaders of these corporations have seen to it that the voices of

¹ Government Service for Land Improvement, Drainage, and Reallocation.

their more skilled and probably more specialized colleagues are now heard in circles formerly dominated by tradition.

Under the influence of these two forces, the state and farmers' organizations, the agricultural community experienced an extraordinarily rapid development during the last 50 years, a development which by no means has reached its peak. Education and advisory work raised the level of professional skill, and farmers' organizations fostered among their members a broader view of their profession and of world relations.

Cooperative action strengthened the economic position of the agricultural community. With an eye to conditions on the world market, unsupported by protective tariffs until 1928, agriculture changed from a trade, built on tradition and on the satisfaction of local needs, to an up-to-date profession founded on scientific experiments and closely interwoven with world economics. The Netherlands is too small to produce sufficient food for its population. Bread grain, coarse grain, and fat must be imported. On the other hand, before the war vegetables and bacon were exported to the United Kingdom and Germany. By growing special crops, which need not only much capital and labor but also great skill, the Netherlands was on its way to becoming the market garden of the industrial regions of Western Europe.

The extremely dense rural population unavoidably led to an intensified utilization of the soil. Advantage was taken of every facility to improve growing conditions by applying the latest scientific knowledge.

In this sphere, modern methods of applying soil science and controlling the water supply were developed. Other branches of agricultural science, all focused on practical application, also showed gradual progress. Fundamental research was evaluated mainly by the practical possibilities it offered. Research was closely allied to practice. Actually, farmers themselves set the example of experimentation, and the difficult problems encountered were tackled by specialists at a much later date. For this reason, a group within the population was keenly interested in soil problems and was inclined to apply, though very carefully, new knowledge in designing their schemes of management. This possibility of utilizing the results of research for practical purposes had a particularly stimulating effect. At the same time it raised the demands made on agricultural science for practical results. The cultivation of science for its own sake, usually resulting from seclusion of the research worker, had only limited prospects.

The Netherlands is a country poor in mineral resources. It does not produce basic commodities in demand on the world market. The national economy must rely on the intelligence of the people and the skill of the workers of all classes. In this respect, soil productivity, raised to the highest level attainable, is a strong pillar of prosperity.

That agriculture could develop to such an important place in the national economy of a country whose welfare had for ages been dependent upon commercial intercourse, is indeed remarkable. That such development was possible was due to a large extent to the tendency of farmers to organize, with the result that the agricultural interests became powerful enough to command respect. This

tendency has existed for centuries. In the Netherlands, an essential object of cooperation was to combat superfluous water. The result was establishment of the catchment authorities. The exciting battle against water has been the immediate reason why farmers, responsible for the upkeep of dikes, always could maintain a prominent place in the organization of the state, even when agriculture as a source of livelihood was reduced to a modest position.

The funds and the man power to fight the battle against water have always been provided by agriculture, even in times of economic depression and even though the existence of the towns also depended upon the outcome. As the farmers in the lower parts of the country have always been able to voice their opinion, they never retreated to the subservient position often held by those in higher regions.

The indispensability of dike-defenses undoubtedly was partly responsible for recognition of the value of the agricultural class in a community dominated by commercial interests. At the same time, it provided agriculturalists with a common interest essential to organization and with a means of self-education.

In the history of agriculture and even more so in the history of regional catchment boards, definite lines of development can be distinguished. These have continued down to the present and help explain the situation today.

HISTORICAL NOTES

When the region now known as the Netherlands first appeared in written history in the 12th century, a fully developed organization for handling water discharge was already in existence. Full economic and judicial powers had been conferred on the catchment boards, who were in charge of the maintenance of dikes, a duty they could not neglect without danger of flooding their own habitations.

The polder organization, the only one in the country with autonomous authority, has pursued lines of gradual development never interfered with by any temporary invader, even men like Napoleon and Hitler. To agriculture, it served as a motive for establishing an authority of its own, for the task of discharging superfluous water has long been of paramount importance to farmers. Even now, there are in this country 2,500 catchment units, administered by the local population, and, as always, many young farmers are being trained in administration by these organizations.

The first impression of the country derived from written history is that the Netherlands was being threatened by inroads of the sea and that agriculture was fighting a fierce war with the water. The most ancient historical records mention many disasters, floods, and dike-bursts, which were all incentives to more intense cooperation. When the sea retreated and the regression resulted in deeper drainage, the productivity of the soil, and consequently also of labor, increased, releasing a great deal of man power. Within a few centuries with the aid of this released man power the community developed an overwhelming prosperity, resulting in the Golden Age of the Netherlands.

The wealth of the merchants in the 16th century expressed itself in the con-

struction of large houses and public buildings requiring much fuel for heating. Peat was used for the purpose. This led to excavation of the peatmoors, which up to that time had been valueless and inaccessible. New land was gained here. Enough money and man power were available to acquire new land also by reclaiming the lakes, and the cultivated area rapidly increased.

Hydraulic engineers of the Netherlands traveled not only throughout the country but all over Western Europe as well. Good will was built up for land acquisition, enclosure of lakes or pools, and land reclamation. This still influences land management to a marked degree. It is this enthusiasm for drainage, peat excavation, and other land improvements that turns the scales when the pros and cons of any land-improvement scheme are considered. We cannot appreciate today's knowledge of soil and drainage without taking into account the consequences of this age-old development.

TABLE 1
*Value of total agricultural output of the Netherlands**
In millions of guilders

CROP YEAR	PRODUCE FROM ARABLE LAND	ANIMAL PRODUCE	HORTICULTURAL PRODUCE	TOTAL	RAW MATERIAL	ADDITIONAL VALUE
1939	155	575	120	850	256	600
1947	456	987	448	1891	202	1689
1948	453	1141	452	2046	341	1705
1949	444	1534	503	2481	452	2029
1950	655	1880	520	3055	564	2491

* Reference: Handbook Central Bureau of Statistics.

GOVERNMENT ACTIVITIES

The influence of the government upon the development of agriculture is of more recent date. When, about 1890, agriculture was involved in a serious depression, the only way to render assistance was, according to the dominating liberal political ideas at that time, to foster advisory work and education. In the following years an agricultural advisory service was established. This now enjoys the full confidence of farmers, and though exposed to much sound criticism has nevertheless found its ideas gratefully accepted.

This very effective advisory service is the key to a clear understanding of the agricultural potentialities of the Netherlands (table 1). The significance of this service to soil science and other research can hardly be overrated. Because of the cooperation of the advisors, it has always been possible to make practical application of the results of thorough investigations. Agricultural education, also established in this period, penetrated to all parts of the country and was taken up by the farmers' sons. As a result, not only has valuable knowledge been spread but good will has been built up for research and advisory work. The importance of this must not be underestimated.

The main contact with farmers in the first decades of advisory work was through the effort to increase use of fertilizers. This gave both teachers and

advisers a hold on the agricultural population. The experiment station at Groningen was established to further research on soil chemistry and fertilizers. The advisory service and this station, in close collaboration, have succeeded, in the course of 50 years of research and publicity, in making the Netherlands one of the largest consumers of artificial fertilizers per unit of area in the world (table 2). Today, the quantity of fertilizers applied depends not on the farmer's knowledge, but rather on his financial position and the supplies available.

In the fertilizer field, no further appreciable improvements can be envisaged under the present systems of husbandry. Improvements will entail merely adjustment of minor errors in the quantities applied and more careful consideration of the variations in available plant nutrients in the soil. To this end, practical farmers can call upon soil-testing laboratories, which annually analyze more than 100,000 samples.

TABLE 2
*Total quantities of fertilizers applied in the Netherlands**
In 1,000 tons

SEASON	NITROGENOUS FERTILIZERS	PHOSPHATIC FERTILIZERS	POTASSIC FERTILIZERS
1924/25	34	88	89
1929/30	61	106	92
1934/35	59	103	82
1939/40	102	108	104
1945/46	76	49	46
1946/47	106	119	68
1947/48	116	137	100
1948/49	115	120	108

* Reference: Distribution Bureau of Fertilizers, The Hague.

In the 19th century the cause of many of the difficulties encountered could not be determined, but today fertilizer problems are solved by applying the results of many field experiments. The problems to be solved have gradually become of less importance but require experiments on an ever-increasing number of plots.

A survey has shown that fertilizer usage in the Netherlands under the present systems of husbandry has reached almost its economical limit.

Such fertilizers as potash and phosphate are applied in adequate, perhaps even slightly excess, quantities. In many cases rich soils are overfertilized and poor soils underfertilized. By increasing the total application of phosphoric fertilizers, of which there was formerly a great shortage, a 1 per cent increase in total yield for the whole country can still be envisaged. It has been calculated that a further increase of 2 per cent in total yield can be anticipated from potash and 3 per cent from lime.

Though for some fields trace elements are of paramount importance, no considerable increases in total yield for the country can be expected from more general applications. For magnesium, the possibilities cannot yet be estimated. The results of investigations with regard to this plant nutrient have only lately

attained the stage of practical application. The benefits from more efficient fertilizing with magnesium might well prove to be more promising than has been presumed.

The position of nitrogen differs slightly from that of other nutrients, as the type of farm management is a more or less decisive factor here. Marked improvements are still conceivable, namely, an increased yield of 10 per cent on arable land and of 40 per cent on grassland. To achieve the latter, however, a radical modification of management will be needed and education and extension will have to prepare the way among the rural population.

More efficient use of fertilizers by adapting the applications to the nutritional reserves in the soil is of considerable economic importance. This does not imply larger applications but more efficient usage, which means profit both to the farmer and to the nation. The efforts of soil scientists in this country are, however, no longer devoted so largely to fertilizer problems. The interest is now focused on other subjects, and more results are expected from studies of soil profiles and of control of water-table levels.

PRESENT OBJECTIVES OF SOIL SCIENCE

During the last few decades more attention has been paid to improvements in soil and in the utilization of water resources. The ever-increasing density of population, particularly the birth-excess of the rural population, and the ever-increasing land hunger are incentives to intensified land use. There is scarcely any reclaimable wasteland left. Most of the terrain not under cultivation is devoted to natural sanctuaries. Recreation areas are likewise debarred from agriculture. The beds of lakes and pools that are suitable for reclamation are already under cultivation. Only the gigantic operation of reclaiming the Zuyderzee presents fresh opportunities, but this operation is beyond the power of private initiative.

Because of the meager possibility of acquiring new land, means of increasing the productive capacity of the land now under cultivation are being emphasized. Attempts are being made to utilize the components of the present profiles in developing new profile structures more valuable to agriculture. Soil science is being applied to finding ways and means of wresting from the soil every last possible scrap of produce.

To make land improvements of this kind is very costly. The expenditure usually far exceeds the funds that can be profitably invested by private capital. It is necessary to consider in detail here the financial aspects of this problem because the importance of the land improvement works concerned cannot be properly appreciated without an understanding of the concept of their financing. In this respect an ever-widening theory is being developed to determine how great an investment of funds granted by the exchequer is justified.

The argument will be based upon the developments resulting from the birth-excess. Many young prospective farmers have long had great difficulty in finding farms. Increased demand and a stationary supply caused land rents to rise more and more, with the result that the price of land also increased considerably.

Consequently, the position of tenants weakened gradually, and even when wholesale commodity prices dropped only slightly, it became critical.

It was found necessary to stabilize rents at the 1940 level. In consequence, selling prices of land also became stable. After the postwar devaluation of the guilder, the prevailing land prices were virtually maintained, and therefore rents and selling prices reached a level far below the commercial value of the land. The support thus given to tenants has become very substantial, but a drawback of the situation is that the cost of improvements is usually not recouped by a higher price when a landed property is sold. The result is that owner-occupiers are prepared to spend money on their land only if the improvements are sure to be very remunerative. Because of the fixed rents, landowners are even less prepared to bear the costs of improvements on tenant farms.

As a result of the artificially low prices, part of the capital invested in improvements does not yield interest, as it would if the price structure of land were not

TABLE 3
*Exports of agricultural produce from the Netherlands in 1949**
In millions of guilders

Pulses.....	7.8	Cheese.....	159.0
Potatoes for industrial use.....	48.1	Condensed milk.....	129.1
Seed potatoes.....	51.5	Milk powder.....	35.6
Flax.....	32.7	Fresh eggs.....	55.5
Agricultural and horticultural seeds..	51.0	Raw vegetables.....	110.8
Potato starch.....	44.6	Fresh fruit.....	59.4
Butter.....	226.2	Bulbs.....	83.4

* Reference: Handbook Institute of Agriculture Economics.

controlled. Consequently, essential improvements are difficult to realize. Simultaneously, conditions developed in which laborers, being unable to find work in either industry or agriculture, were employed in land improvement. Particularly in the thirties, unemployment was rife, and more and more unemployed persons had to be considered. In subsequent years conditions changed, and only local seasonal unemployment had to be taken care of.

Economic conditions in the Netherlands do not warrant much mechanization of soil-improvement work. Careful discrimination between the layers in the soil profiles demands more accuracy than is possible with machinery. For these reasons the use of unemployed labor to carry out land-improvement schemes of the character cited is a practical proposition.

Another point is that the national economic interests of the Netherlands are well served by increases in agricultural production.

Industrialization of the countries formerly producing raw materials will, in the long run, inhibit industrialization in Western Europe, and more attention will have to be paid to agriculture. Right now, however, export of industrial products is difficult and furnishes insufficient exchange to pay for the imports (tables 3 and 4). Increased agricultural production, therefore, can favorably affect the balance of trade.

Finally, it should be pointed out that 50 years of education and advisory work have resulted in a skilled population, able to utilize land improvements effectively.

Appreciation of the significance of moisture in the soil and of water in the ditches during ages of catchment activities in this country provided a basis for taking advantage of the fresh opportunities for land improvement, which means improvement of water-holding capacity, presented by the new ideas on financing.

If one divides the task of soil science into practice and research, then applied soil science will be devoted to meeting the need for more agricultural produce and for more or less temporary objects for employment of seasonal surpluses of labor. Research in soil science will undertake to define the fundamentals of the productive capacity of soils and show where definite improvements can be made.

TABLE 4
*Home production and imports of some important commodities of the Netherlands**
In millions of kilograms

YEAR	WHEAT		OTHER CEREALS		SUGAR	
	Home grown	Imports	Home grown	Imports	Home grown	Imports
1938	434	644	1138	1177	222	133
1947	194	489	835	431	223	-48
1948	305	615	836	767	201	124
1949	425	432	1129	750	256	144
1950	297	624	1024	937	367	92

* Reference: Handbook Central Bureau of Statistics and monthly publications of statistics.

The most suitable depth of drainage, the necessity for leveling, and the breakup of hardpans must be indicated, and the areas involved must be defined. The activities of the state in establishing economic conditions conducive to this work require due consideration of the financial prospects. This means that the investigations must be directed particularly to increases in cash returns from the improvements. The complex relations of soil, water, and crops must be surveyed.

This comprehensive task, involving the difficult study of factors that cannot be changed at will on an experimental field, has been taken in hand by various institutions. The complexity of the problem suggests uncertainty that the present generation of investigators, like the preceding one, will be able to advance the understanding of problems of land improvement so much that in the near future it will be possible to say that no further major increases in national income can be expected from land improvement.

SIGNIFICANCE OF LAND-IMPROVEMENT WORKS AND GRANTS

As already mentioned, the financial administration of land-improvement works constitutes a very important part of drainage and reconditioning activities.

Without financial support, it would be impossible to find many projects that could be taken in hand. Under prevailing conditions, the more important possibilities of improvement yield inadequate profit.

As long as unemployment was rife and relief work was essential, the returns from a labor project were not a primary consideration. Today the number of unemployed is not high, but still land improvement and regional drainage works must be executed. In contemplating the granting of subsidies, the question has arisen whether relief of unemployment should be a decisive consideration. The conclusion reached is that the execution of subsidized schemes even by employing regular workers is in the national interest.

This conclusion is based on the consequences of the war devastations, the rapid increase in population, and the high level of crop yields which are capable of only very slow further advances. One of the consequences of the war was a disturbed balance of trade, the inflationary action of which necessitated efforts to maintain

TABLE 5
*Population and its density in the Netherlands**

YEAR	NUMBER	DENSITY PER SQ. KM.	YEAR	NUMBER	DENSITY PER SQ. KM.
1879	4,012,000	123	1940	8,923,000	271
1889	4,511,000	138	1946	9,542,000	286
1899	5,104,000	156	1947	9,715,000	291
1909	5,858,000	179	1948	9,884,000	296
1920	6,865,000	210	1949	10,025,000	309
1930	7,935,000	243	1950	10,200,000	315

* Reference: Handbook Central Bureau of Statistics.

a low price level to prevent an excessive rise in wages. A rise in prices of agricultural produce is being counteracted as much as possible, and a scheme of subsidies has been adopted to avoid it.

The increase in population (table 5) gives rise to many difficult problems. It is very doubtful, indeed, whether agriculture can continue to absorb a substantial number of these new workers. Industrialization on a large scale will, as a matter of fact, be essential, but it is very difficult to visualize where purchasers of manufactured articles could be found abroad. The expansion of agriculture, however, might result in production that could replace imports from foreign countries. It could create means of subsistence for the anticipated excess in population, whether or not these compatriots could grow the produce themselves. Furthermore, these commodities would not have to be bought abroad, and foreign currency to pay for them would not be a problem.

Finally, the annual increase in labor productivity in agriculture is not quite 1 per cent. This is only a third of the rate for commerce and manufacturing industries. Increase in labor productivity by employment of less labor would necessitate finding employment elsewhere for the replaced workers and would lead to an increase in the surplus of labor. In this direction no solution to the problem

can be found. In addition, the profitability of mechanization is limited, because of the price structure and the unsuitability of the culture of refined crops to mechanized farming. Total yields would not be greatly increased by mechanization. It is envisaged that in the next 20 years the population will increase by 1 per cent annually, and therefore a decline in agricultural imports can hardly be anticipated. The danger from more rapid development of labor productivity in industry is that agriculture will lag behind. If agricultural productivity increases annually by 1 per cent, compared with 3 per cent in the industries, then something must be done to maintain the balance.

A rise in commodity prices will be necessary, but this is not desirable because of its influence on the relation between wages and prices.

An alternative is to aim at a more rapid development of soil productivity by the inception of schemes designed to effect an accelerated rate of increase in production. As a whole, this will involve investment of fresh capital. Owner-occupiers, using 50 per cent of the land, are not prepared, however, to supply the needed capital because the fixed rents and sale prices of land do not make such investments profitable.

Prospective workers will have to be employed somewhere, and if the prosperity of the rural population lags behind that of the urban population, assistance will have to be furnished. Finally, as price controls prevent adequate returns to owner-occupiers, the government must assume the task. The necessity for granting subsidies arises from the need to supply work to the increasing population and maintain the present standard of living.

POSSIBILITY OF GREATER PROSPERITY THROUGH LAND IMPROVEMENT

It can be assumed that the monetary return from 1 hectare of land will support one inhabitant of the Netherlands. If one takes into account the increase in population to be expected, it will be clear that a considerable part of the population increment must find employment in either commerce or manufacturing industries (table 6).

It might be assumed that the most convenient solution would be to find occupation for 10 per cent of the increased population by expansion of agriculture. If that could be attained, the composition of the population, classified according to occupations, would not change substantially. In addition, it might be assumed that half the difference between the increase in labor productivity in agriculture and in industry can be met by a rise in prices of the agricultural produce. The other half would have to be covered by increases in labor productivity.

Experience shows that ultimately an increase in the production of land already under cultivation, equal to the yield of 1 hectare, demands a capital investment of 5,000 guilders. For a proper understanding, it may be well to point out that increments in production are preferably expressed in yields equal to that of a hectare, as a monetary evaluation of the improvements becomes possible by assessing the apparent gain of land.

A survey is possible on the basis of these fundamental data. The agricultural income must rise by 1 per cent a year. This means an increased yield equivalent

to that of 24,000 hectares, if the total area of cultivated land is 2,400,000 hectares. This would require an expenditure of 120 million guilders annually, if the cost of improvements, representing the yield of 1 hectare of land, is estimated at 5,000 guilders. If additional capital of 120 million guilders were invested annually, it would be possible to accommodate the part of the anticipated increase in population that should obtain its livelihood from agriculture. Most of the area of cultivated land would have to be subjected to radical improvements, not counting those made by farmers on their own initiative, for this normal increase is included in the annual rise of 1 per cent a year in labor productivity.

If the intention is to furnish occupations in agriculture to another 10 per cent of the envisaged increase in population, equal to 2 million head, of which half

TABLE 6
*Number of workers in the Netherlands classified according to occupations**
In thousands

OCCUPATIONS	1938	1946	1947
Manufacturing industries.....	1090	1260	1400
Agriculture.....	640	640	640
Navigation.....	30	30	30
Commerce.....	430	440	460
Transportation.....	300	340	370
Domestic services.....	270	150	180
Education.....	50	60	60
Civil services.....	70	200	180
Army and Navy.....	30	110	170
Other occupations.....	130	180	190
Total.....	3040	3410	3680

* Reference: Oomens and Van der Kolk: Stat. and Econ. Inv. No. 4, 1949.

will be active workers—the other half being women, children, and elderly people—then a primary income of 10 million guilders will be involved (table 7).

Based on a return of 700 guilders per hectare and taking the results of completed improvements as equal to 25 per cent of this amount, the extra income can be realized by improving 57,000 hectares annually. By estimating the investment required at 1,200 guilders per hectare, the total amount of capital needed will be 70 million guilders.

This calculation reflects the task that will be assigned to agricultural science by the community in the economic sphere. A total investment of 190 million guilders a year would imply that 160,000 hectares of land already in cultivation must be taken in hand annually, or that 20,000 hectares of new first-class land must be acquired by reclamation every year. In the case of reclamation of wasteland, 40,000 hectares would have to be added to the cultivated area annually.

A plan developed from these three possibilities would have to cover 20 years, as it is presumed that after that time the Dutch population will have become stationary.

The expenditure of some 200 million guilders annually would probably be acceptable. But finding the land for these improvements presents some difficulties. Some 230,000 hectares of lakes, seas, and tidal washes are still available for reclamation (table 8) and would satisfy the requirements of agriculture for 11 years. The area of wasteland to be considered for reclamation is 50,000 hectares, which would meet the needs of agricultural expansion for only 1 year. To satisfy

TABLE 7
*National income of the Netherlands according to occupations**
In millions of guilders

OCCUPATIONS	1938	1947	1948
Manufacturing industries.....	1,493	4,224	4,982
Agriculture.....	332	1,267	1,434
Fisheries.....	11	53	42
Commerce.....	525	1,438	1,720
Transportation.....	501	1,065	1,179
Banking and insurance.....	154	371	398
Education.....	136	280	383
Other occupations.....	512	706	686
Utilization of real property.....	641	580	558
Civil services.....	257	1,100	1,096
Occupations abroad.....	402	233	294
Total.....	4,964	11,317	12,772

* Reference: Handbook Institute of Agricultural Economics.

TABLE 8
*Area of wasteland in the Netherlands**

YEAR	HECTARES
1900	591,000
1910	543,000
1920	482,000
1930	378,000
1940	270,000
1950	210,000

* Reference: How the Netherlands Expanded; 10th anniversary of the CTD. 1945.

the demand for the remaining 8 years, another 1.3 million hectares of land already in cultivation would have to be subjected to improvements resulting in yield increases. Such a development would represent improvements in the control of water resources, in the productive features of soil profiles, in efficiency of fertilizer treatments, and in land utilization.

It is hardly imaginable, however, that such a comprehensive scheme could be completed within 20 years.

Obviously, there are several solutions for the difficulties arising from the

rapidly increasing density of population and the diminishing returns from endeavors to intensify agricultural production. One of these solutions is a marked stimulation of industrialization, and another one is emigration. We are interested, however, only in the task that could be assigned to agricultural science, more particularly to soil science. This task must include determination of the best paying methods of improvement and also of the methods assuring the highest net returns.

As already mentioned, one must not acquiesce in the adaptation of production to prevailing soil and water conditions. Rather, all opportunities for adapting growth-promoting factors to the required crops must be traced and thoroughly utilized. Numerous possibilities offer themselves. It may be practical to achieve improvements by more efficient fertilizer treatment, by growing improved varieties of crops, by using more advantageous rotations of crops, by acquiring new land, by realizing higher yields through better control of water resources, by ameliorating soil profiles, and by better management of soils and crops by the farmers.

Most of these improvements are already receiving considerable attention, and any intensification will be difficult to effect. As to land improvements, the position is different, though here, too, any considerable expansion of the magnitude of the work already being done will be difficult to achieve. On account of the wide experience gained with many methods of land improvement, experience that is constantly being added to, it is scarcely imaginable that the necessary know-how will be wanting if it is needed in the future to help maintain the standard of living.

It is inspiring to workers engaged in land improvement and drainage to be able to furnish so much help in maintaining the standard of living of the agricultural community. The opportunity offered to them to implement schemes and to perform an essential scientific task of very high standard should, however, not be considered as a consequence of unusual activity of, or of special knowledge accumulated by, the organizations, institutions, and workers. It is the very extraordinary social and economic conditions that demand these exertions in the sphere of land improvement.

The Netherlands can be assured that at the proper time she will have at her command a panel of soil science workers whose practical and research activities will meet the high requirements arising from conditions prevailing in her realm.

SOILS

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Alluvial soils comprise about 50 per cent of the soils of the Netherlands. The most prosperous areas of rural Netherlands have developed on these fertile soils. The traditional concept of the Netherlands being won from water in an age-old struggle applies especially to the lowlands, which have been formed entirely of alluvium.

In most countries, alluvial soils have attracted less attention than residual soils. The latter are of greater interest to the soil scientist because they show the result of interactions of the five soil-forming factors: parent material, climate, vegetation, topography, and time.² Most alluvial soils are very young and show little effect of soil-forming factors. Long ago a famous Russian soil scientist of the pedogenetic school who was visiting Holland was so disappointed with what he saw of the alluvial soils of the province of Groningen that he exclaimed: "These are not soils." But the grand old master of the Dutch soil scientists, Dr. D. J. Hissink, gave this answer: "Perhaps they are not soils, but they produce crops." Actually, the young marine clay soils of the Netherlands are among the most productive soils in the world and, from the standpoint of food production, similar soils elsewhere deserve the full attention of soil scientists, agronomists, and rural planners.

The high productivity of alluvial soils can be utilized only after proper reclamation. Many coastal swamps of all continents have high potential fertility. Whether this fertility will ever contribute to world prosperity will depend primarily on the drainage technique employed.

Drainage and reclamation of coastal swamps is a national art of the Dutch. From the Middle Ages up to the 20th century, Dutch experts reclaimed swamps all over the world. When we visit such old reclamations in foreign countries we at once recognize the Dutch technique, but we often observe also that later management, especially maintenance of the drainage works, has been defective. To be productive, alluvial soils not only must be properly reclaimed, they must also be properly managed. The accumulated experience of the Dutch in the legislative and administrative fields is as important as their technical tradition.

MARINE ALLUVIAL SOILS

The marine alluvial soils of the Netherlands are by no means uniform. Their profiles reflect the very different ways in which they have been formed. Much of the differentiation of properties of the horizons is due to the principles of sedimentation. Soil surveyors in the Netherlands have found that good maps of alluvial soils can be made only if the formation of the deposits is understood.

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² In countries with an old civilization, a sixth factor, man, is of as great importance as the classical five.

The relation between geology, especially sedimentation, and soil science is most apparent in such soils.

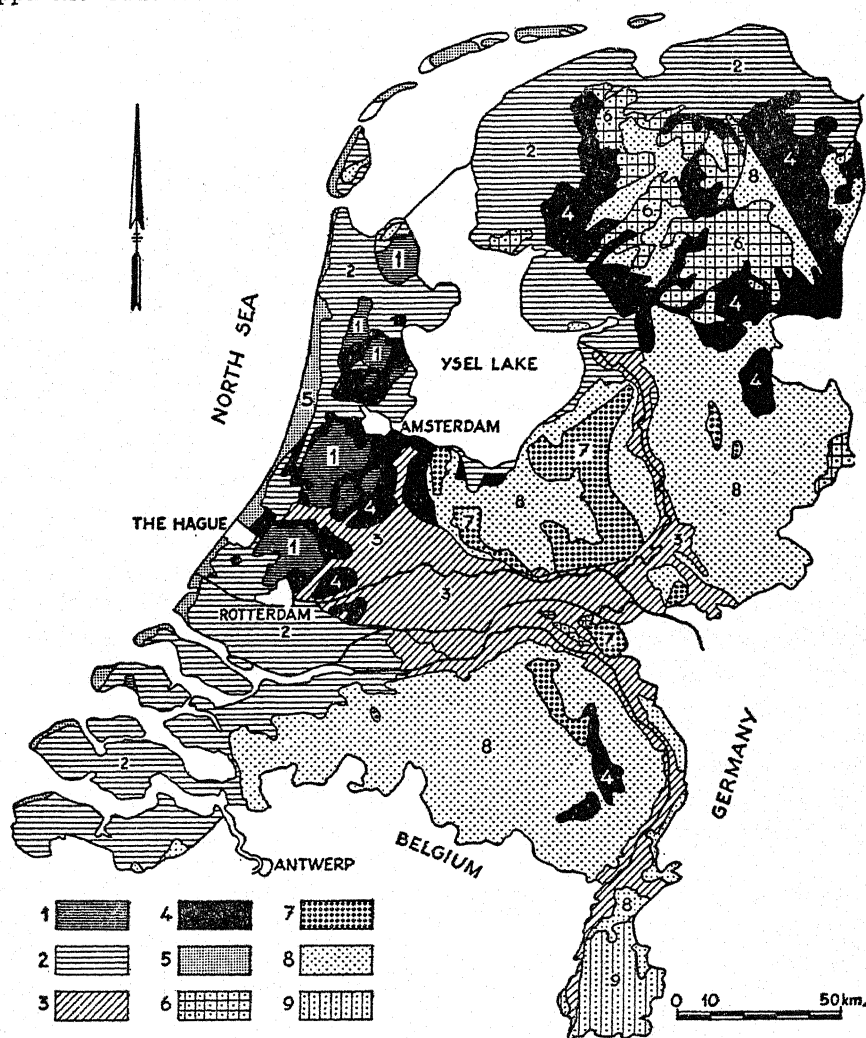


FIG. 1. MAP OF THE SOILS OF THE NETHERLANDS

1. Old sea clay soils; 2. Young sea clay soils; 3. River clay soils; 4. Peat and peat reclamation soils; 5. Dune sand soils; 6. High, moist, sandy soils; 7. Gravelly sandy soils; 8. Various sandy soils; 9. Loess soils.

The intricate patterns of silted tidal creeks, as shown on the soil maps of Westland, South Beveland, and Walcheren, explain the distribution of lighter and heavier soils. Many, but not all, young alluvial marine soils are rich in CaCO_3 . Some of them are rather heavy, sometimes sticky clays.³ In the older

³ The term *clay* is used in this paper as an equivalent of the Dutch term *klei*. The Dutch designate as *klei* all young deposits of the sea and the rivers, from sandy loam to clay.

literature it is taken for granted that such soils originally were rich in CaCO_3 like ordinary marine soils. The beautiful structure of such soils is supposed to have been destroyed and their CaCO_3 lost through leaching under the influence of the moist climate of the Netherlands. The heavy, sticky clay soils have even been considered as podzols on marine clay. Recent studies indicate that this view is wrong and that the heavy marine clay soils that are poor in CaCO_3 have never been calcareous. Most of the heavy, sticky marine clay soils are utilized for grazing. They are less productive than the younger calcareous marine clay soils, but they are good enough to support the highly productive Frisian cattle.

Some of the alluvial clay soils of the brackish belt were deposited as black muds, poor in CaCO_3 but rich in FeS_2 . After drainage, these muds oxidize and form very acid soils, containing free H_2SO_4 . This so-called cat clay presents one of the most troublesome problems in coastal reclamation. Along the present coast and estuaries of the Netherlands there are no instances of the formation of such muds, but in the natural landscapes of the past they were not infrequent.

In many coastal areas of the world, similar very acid marine soils occur. They have not received sufficient attention. Textbooks on soils do not describe them.

Over large areas, the marine clays of the Netherlands cover peat deposits. After drainage, the peat subsoils become compacted, and the land surface settles. Where the peat layer is absent because of former erosion of the peat by the sea, there is very little compaction but, rather, a differential settling, which is known as inversion of the topography. The resulting irregular topography is a nuisance in the regulation of drainage.

The extensive peat deposits of the western part of the Netherlands cover an older sea clay deposit, which ordinarily lies 12 to 15 feet below sea level. As about 250,000 acres of this peat layer have been excavated for fuel or removed by marine erosion, many lakes are formed with bottoms consisting of the old sea clay. Most of these lakes have been reclaimed in the course of the centuries, and now the former clay bottom is farmed. Many of the old sea clay soils are excellent, but a rather large part is composed of cat clay. Fortunately, the topsoil of most of the cat clay is a black mixed soil deposited on the bottoms of former lakes. Ordinarily, these black soils are used for intensive grazing.

RIVER CLAY SOILS

The big rivers Rhine and Meuse, which divide the country into a northern and a southern part, have also formed alluvial soils. Bordering ancient branches of these rivers, natural levees of brown and permeable clay soils are found. These natural levees surround lower basins, the backswamps of the natural landscape, with extremely heavy, impermeable, gray clay soils. The higher land on the levees was reclaimed before embankment, which was terminated about 1200 A.D. The backswamps were parceled and drained a century later. Free drainage by sluices was followed by windmill drainage, and during the 19th century the windmills were replaced by pumping stations. Among the higher, brown, permeable river clay soils are many of the best orchard soils of the country. The basin clay soils, however, are rather unproductive. Their drainage raises

very difficult problems, as they periodically suffer from drought and from excessive wetness.

Proper drainage of the whole district is adversely influenced by the seasonal regime of the rivers. During wet seasons, when drainage is most necessary, the rivers between the dikes are much higher than the land surface. Under these conditions, water from the river seeps through the coarse sandy subsoils into the land, thus increasing the quantity of excess water. At the same time, drainage to the high river level is especially difficult. During dry seasons, when the rivers are very low, the opposite process takes place: there is already a shortage of water for the crops, and the rivers drain the sandy permeable subsoil of the region so heavily that the shortage becomes even greater.

Under such conditions the best soils are those that are permeable and at the same time retain enough water in their subsoils. Such soils are the valuable orchard soils on the natural levees.

In the western part of the river clay area, peat underlies the heavy, sticky clay soils. Because of inversion of the topography, such soils are now about 6 feet lower than the narrow clay strips bordering the rivers. This differential settling, like marine inversion, causes much trouble for the drainage schemes.

SANDY SOILS

The sandy soils, including peat soils found in depressions of the sandy area, comprise about half the surface of the Netherlands. About 80 per cent of the sandy materials near or at the surface in the Netherlands were formed as wind-blown deposits at the end of the Pleistocene epoch. They are called *coversands* and are the sandy equivalent of the loess deposits found elsewhere.

The coversands are of two types: rather pure wind-blown sands of uniform but varying grain size, and sands more or less rich in silt. The latter are mixtures of coversand and loess and are ordinarily called *loamy coversands*.

Other sandy soils are of mid-Pleistocene age and are partly of glacial origin. Many of them contain gravel and some finer material; such sands are poorly sorted, in contrast with the wind-blown sands. The sandy regions have a gently rolling topography. Some hilly tracts rise to about 300 feet above sea level.

On all these sands, soil profiles have developed since the Pleistocene. On the pure sands, podzols have been formed under influence of a heath vegetation. The gravelly sands, with their low content of fine particles, show forest soil profiles of the gray-brown and brown podzolic kinds. This is also true for the finer coversands, especially the loamy sands.

As a whole, these soils are rather infertile. When stone-age man settled in this area he could practice only extensive grazing and some shifting cultivation. Thus, much of the forest was destroyed, and extensive heath fields came into being. Later, man found permanent agriculture possible by maintaining large numbers of livestock, especially sheep, collecting the dung, and manuring a very limited area of permanent arable land. This old arable land is characterized by deep black soils and is found near all the villages and hummocks in the sandy parts of the Netherlands. The heath plains and forests were grazed and were

impoverished by man's use of the heath sod and the forest litter as bedding in his barns. It is not surprising that heath soils were considered as the poorest of the poor soils up to the last quarter of the 19th century. The reclamation of these heath soils is a great achievement, but it has been made possible only by the introduction of chemical fertilizers.

Water conditions rather than lack of plant nutrients are the bottlenecks of agriculture in these parts of the country. When the soils are too high above ground water, they are of no use to agriculture and are better suited to forestry. When they are too wet, they can be drained and used for pasture. Between these two limits, various qualities of arable land are found. The classification of these soils is based on the depth of the top of the glei horizon in relation to the thickness of the humic upper profile and to the content of fine particles. In pure sands with an average humus content, a glei horizon depth of 5 feet means land of inferior quality. A depth of 2 feet would be optimal for arable land, and 1 foot is the limit of arable land on the moist side.

It is impossible to use the water table itself as a mark in soil surveying and classification, because it fluctuates too much during the seasons and this makes regular field work impossible. The glei horizon gives a reliable over-all picture of ground water conditions in the soil profiles.

On the driest sandy land, only rye can be grown. Slightly better soils produce two crops in rotation, rye and oats. On still moister land, potatoes also can be grown. Good sandy arable land is characterized by a four-crop rotation, including mangolds. The farms are small and managed in such a way that the products of the arable land serve as fodder for the livestock, which is also supported by the pastureland on the lowest soils.

In the northern part of the country the coversands rest on glacial till, which strongly influences their water conditions. Such soils have been described as high moist sandy soils.

Part of the Pleistocene sand landscape has been destroyed by ancient wind erosion. The inland sand dunes, formed in this way, have been stabilized by forestation, but some of the dune sand is utilized for agriculture, often with rather pitiful results. Small areas of these inland dune sands are moist and well suited to market gardening.

PEAT SOILS

Peat soils are found in the low western part of the country and in flat parts of the sandy regions. The low-lying peats of the west have settled by compaction, and their surface is now about 6 to 8 feet below sea level. They are utilized for dairy farming. Most of the farms consist entirely of grassland. Some favorable parts of the peat region are used for intensive horticulture.

More important is the ancient peat exploitation. In this low land the peat was excavated by dredging, and the many lakes resulting from the dredging were later drained and reclaimed.

The large peat deposits of the flat parts of the sandy regions were wasteland before they were exploited. By digging canals, it was easy to drain these peats,

which lay several meters above the surrounding landscape. Fuel was prepared by cutting the slightly drained peat. The result of the exploitation was not a lake but a sand plain, the sand being the geological substratum of the peat. This sand plain was not bare, because some parts of the peat profile were not good enough for fuel and were thrown away by the cutters. Later this loose organic layer was covered with about 4 inches of sand. The plow mixed the sand with the top of the organic layer. This soil will produce crops only if properly fertilized, but many of these *moor-colonial* soils are excellent. Thus, large tracts of waste moorland have done double duty, first, by producing an economic supply of fuel, and second, by providing very good farmland. We know of no similar example of successful reclamation of peat deposits in the world.

In other parts of the country, peat was excavated in a less systematic manner. Here one finds the usual desolate combination of deep pits and remnants of peat, characteristic of most peat exploitations. It is scarcely possible to reclaim such deserted areas.

DUNE-SAND SOILS

Much of the coast of the Netherlands is formed by sand dunes. Some of these are bare or are covered only with sparse natural vegetation; others have been planted to forests; and still others are grazed. Near the coast, the dunes are young, with no profile development, and mostly calcareous, but the landside is formed by an older dune system, which is strongly decalcified and shows podzol and forest soil profiles similar to those on the Pleistocene sand deposits.

As a whole, the agricultural importance of the dune area is so limited that it would not be worth consideration in this paper if some extremely good man-made soils had not been formed from it. The main reasons why dune sand in its natural state cannot be farmed successfully are that it is too poor and too dry. But lack of fertility is no longer an objection, since the soil can be manured or fertilized, and drought can be controlled by excavating the sand to such a level that the water table is at a favorable depth. It is in this way that the precious flower-bulb soils have been made from dune sand. The ground water in such soils is kept constant during the year at about 55 cm., a deviation of 5 cm. in either direction being too great. Along other parts of the coast, where it is impossible to maintain such a stable ground-water level, good market-garden land has been made from the dune sands.

LOESS LOAM SOILS

A small part of the Netherlands is made up of Pleistocene loess. The soils on these loess deposits are decalcified. Their profiles consist of rather uniform brown loams, with the characteristics of gray-brown podzolic soils. Their reclamation dates partly from prehistoric times.

WATER CONTROL

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It is well known that a large part of the Netherlands is only slightly above sea level or even below and must be protected by dikes against inundation. Moreover, the Dutch climate is moist, and large quantities of excess precipitation must be removed. Flood control and artificial drainage, therefore, are essential for the habitability of the low-lying areas.

Notwithstanding the excess water, investigations have revealed that during dry summers crop production may be seriously hampered by drought, and fresh water is urgently needed. This need could be met if the excess water that is drained into the sea during the wet period in winter could be stored for use in summer.

Storage of water may also prove to be the solution to another problem. The salt waters of the North Sea are gradually penetrating the Netherlands, seriously threatening agriculture, especially horticulture. This invading salt water might be forced back by a stream of fresh water, which in summer could be drawn, at least partly, from storage basins.

CLIMATE

The climate of the Netherlands, being greatly influenced by the proximity of the Atlantic Ocean and the North Sea, is generally moist and temperate, with some frost in winter and a rather cool summer. The mean temperature is 2.6°C. in January and 18.2°C. in July.

The rainfall averages 715 mm. a year, varying from 400 to 1,000 mm. It is well distributed over the months. The precipitation averages 40–60 mm. a month from January to June and 60–80 mm. from July to December. Very wet months, however, may have more than 200 mm. of precipitation, and dry periods of 10 or more days may be expected every summer.

Daily maxima of precipitation may reach more than 80 mm. in summer during thunderstorms. In winter, the critical period for drainage, the maximum rarely exceeds 30 mm., and for several consecutive days the average rainfall is seldom more than 15 mm. a day.

Few data are available on evaporation and transpiration from arable land and pasture, but the results of different observations all point to values between 450 and 650 mm. annually, the exact figure depending on the amount of available moisture as well as on the crops grown. In winter (November–February) the evaporation is negligible, and nearly all precipitation has to be removed. In summer (May–September) the transpiration exceeds the rainfall. In some cases, therefore, the crops may suffer from drought, as their transpiration during the growing period is about 3–4 mm. a day.

¹ State Agricultural University.

The excess of precipitation over evaporation in winter amounts to about 300 mm.; in summer the shortage of water may be estimated at about 150 mm.

TOPOGRAPHY

Topographically the Netherlands can be divided by an imaginary line between the towns of Bergen op Zoom in the southwest and Groningen in the northeast.

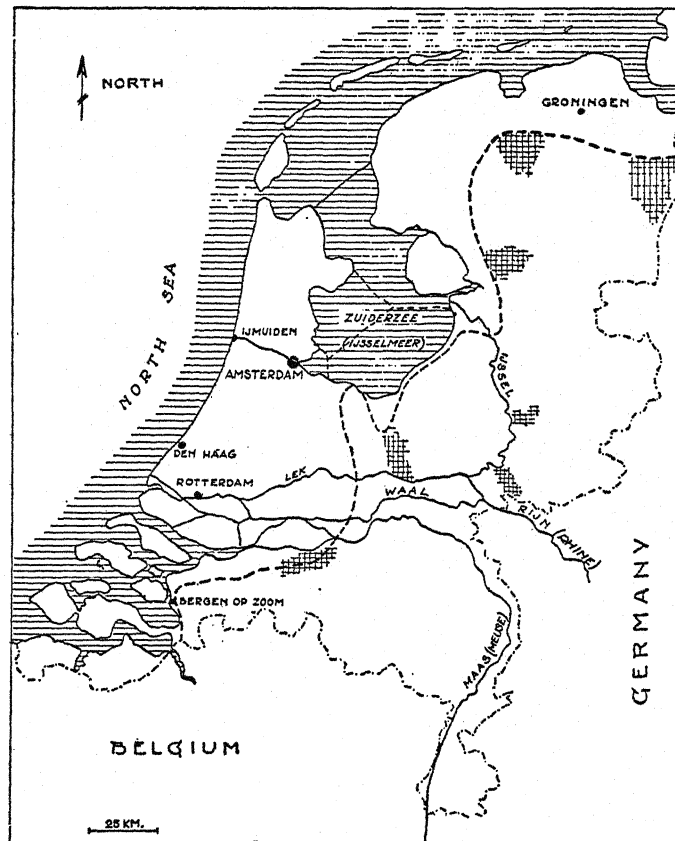


FIG. 1. GENERAL MAP OF THE NETHERLANDS

The dotted line divides the country into a high eastern part and a low western part. Crosshatching marks relatively low areas that suffer from excess water coming from the higher-lying soils.

This line, indicated in figure 1, divides the country into a low-lying, almost entirely flat area in the west and higher, more undulating ground in the east. The higher part of the Netherlands is intersected by the main rivers: the Rijn (Rhine), with its branches Waal, Lek, and IJssel, and the Maas (Meuse). The valleys through which these rivers flow have the same aspects as the low-lying areas in the north and west of the country. Strong embankments protect them against inundation. The high soils above these bottomlands are not directly influenced by the water of the rivers.

When early inhabitants sought places to settle in the Netherlands, the higher areas offered the best opportunities for living and for communications, though as a rule their soils were dry and were low in plant nutrients. On the other hand, the low-lying soils, composed mainly of clay and peat, were generally more fertile and therefore better suited for agriculture. A great drawback was their low situation in a delta region. Being almost impassable, marshy, and often flooded, they could not be put under cultivation until the inundating water, invading the country from the rivers and the sea, could be kept out. As a consequence of the desire to reclaim these very good soils, a complicated system of embankments, drainage works, and polders was developed. Without these works, water control in these areas would have been impossible. Even the landscape is strongly influenced by these works: ditches, canals, dikes, and pumping stations dominate the low and flat countryside.

REMOVAL OF WATER FROM THE HIGH AREAS

The discharge of excess water from the high soils in the southern and eastern parts of the Netherlands is not very difficult, as these gently sloping districts lie 10 to 200 m. above average sea level. Because of their undulating surface, the soils in these areas possess locally a fairly large capacity to store water. Natural brooks and little rivers, running through small valleys, carry the water to the main rivers or to the sea. The proximity of either a river or the sea facilitates the discharge of water from the high soils.

But many of these small streams run a long distance through rather low country before emerging into the sea or a large river. In some cases the lower course of such a stream forms a part of the drainage system of the lowland, thus adding water to an area that may already have difficulty discharging its own water. Some of the areas that suffer from this drawback are indicated in figure 1. The construction of embankments along the lower courses of these streams and the separation of the drainage systems of high and low grounds offer a solution to this problem. Sometimes a pumping station has to be built.

In the high districts the brook-valleys were often flooded, as the water-carrying capacity of the streams and their small tributaries was too low. Between 1920 and 1940 many brooks and small rivers were enlarged, and numerous meanders were cut off. Such improvements are still being made along the smaller branches of these brooks.

Improvement of drainage conditions may lead to damage by drought during summer. A carefully designed equilibrium between the discharge and retention of water is required in these watersheds. This problem is receiving much consideration at present.

An exception to this general picture of the removal of excess water from the high soils is that of the reclaimed peat districts in the northeast. As described by Mohrmann elsewhere in this issue, the original peat layers in these districts were excavated and used as fuel. Afterward the underlying sandy soil, covered with remnants of peat, was reclaimed for agricultural use. In the process of excavating and reclaiming these moors, shipping played a dominant part, as the

fuel was carried to the cities by barges. An extensive system of canals was dug, and these now serve for drainage purposes as well as for inland water traffic.

PROTECTION OF THE LOW COUNTRY AGAINST FLOODING

Greater difficulties were met in the low, flat areas of the north and west. Here water control has gradually been established by development of a complicated drainage system. This forms a pattern that can be understood only from a

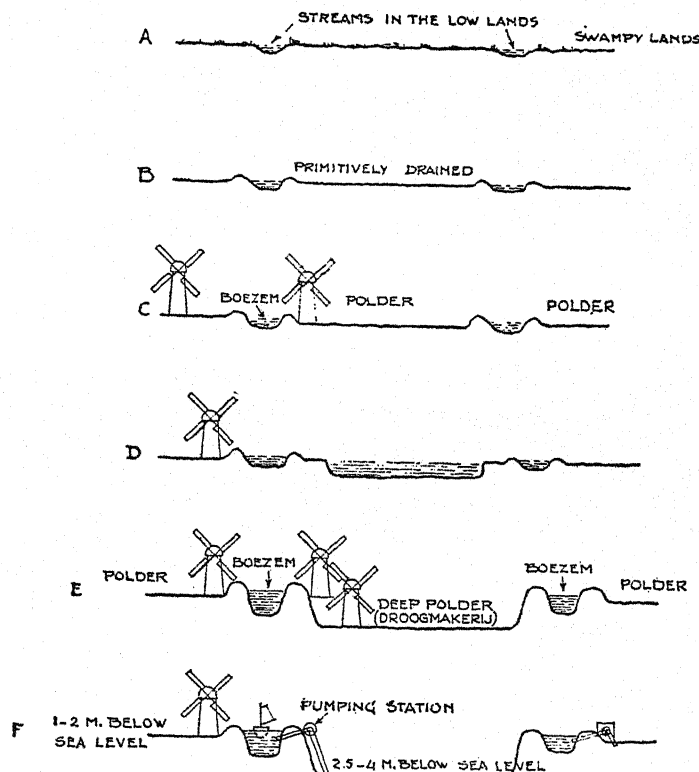


FIG. 2. DEVELOPMENT OF THE DUTCH POLDER COUNTRY

A. Before occupation by man. B. After damming of the streams at their mouths and their embankment; separation of "boezem" and "polder" by small dikes. C. Subsidence of the peaty polder soils and pumping by windmills. D. Digging out of some polders for peat making. E. After draining of the lake originating from peat making. F. Present situation.

historical point of view. Most striking in this respect are the areas lying behind the coastal dunes of the North Sea.

The dunes offer an effective protection against the sea, but originally the areas behind them were often flooded by water from the main rivers. Moreover, the rain falling in the area itself had to be carried off. Broad, slow-moving streams, like Amstel and Rotte, carried the superfluous water into the main rivers and the sea (fig. 2A). On the other hand, they provided entries for flooding waters in case of high sea or river levels.

The first activities of man were directed against these floodings. About 1100 A.D. simple embankments were thrown up along the main rivers, and the streams were dammed at their mouths. Settlements commonly sprang up near such dams. The settlement at the mouth of the Amstel developed into the city of Amsterdam, and that at the mouth of the Rotte, into Rotterdam.

Thus the streams were separated from the waters outside and formed inland water systems, covering large areas (50,000-100,000 hectares). These *boezem* systems, as they are called in Dutch, could discharge their excess water at low tide through sluices in the dams. Often, however, prolonged high levels occurred, causing flooding of the land along the *boezem* waters.

To protect the land from these inundations, small embankments were constructed along the inland waters, a process that was almost completed about 1500 A.D. This resulted in a pattern of small units surrounded by small dikes, called *polders*, each covering an area of about 100 to more than 1,000 hectares. They sluiced their water into the *boezem* system at low *boezem* levels, the *boezem* acting as a storage basin until the water could be sluiced into the main rivers or the sea (fig. 2B).

FURTHER DEVELOPMENT OF THE POLDER COUNTRY

Though this system of polders and *boezems* contributed much to the water control, it was by no means perfect, as the excess rain water from a polder could be evacuated only at low *boezem* levels, and the *boezem* itself could discharge its water only when the water level outside was low. Often the rainfall inundated the land in winter and the soil remained waterlogged until late in spring. Moreover, this situation grew gradually worse as the measures taken to drain the land caused a subsidence of the soil, which in many of these areas was peaty. The surfaces of the polders were lowered by this process, and the maintenance of a sufficiently deep water table grew more and more difficult. The situation was aggravated still more by the relative rise of the sea level with respect to the level of the land, which gradually hampered the discharge of water.

A great improvement was brought about in the 15th century by the invention of the windmill and the paddle wheel. With these, the water of a polder could be pumped into the *boezem*. This pumping accelerated the rate of subsidence of the soil, so that today most polder soils lie far below the *boezem* levels to which they formerly drained their water freely. This process is illustrated in figure 2B and C. Only modern pumping techniques, developed in the 19th and 20th centuries, could solve the difficulties arising from this situation. The use of steam engines, followed by electric and Diesel engines, together with modern pump construction had a large share in this improvement. These engines also enabled large quantities of water to be pumped from the *boezems* into the main rivers and the sea, thus resulting in better control of the *boezem* levels.

In addition to soil subsidence, a still more marked lowering of the surface in some places was caused by human activity. The increasing population of the western part of the Netherlands, which had no access to vast forests, began to excavate and dry the peat soil for fuel. Seldom has a population more literally undermined its source of livelihood. In the course of about five centuries nearly

all the peat suitable for combustion has been dredged away and turned into fuel. As a rule, this peat digging took place polder by polder, so that within the limits of such a polder the land was turned into a lake several meters deep (fig. 2D).

In the 17th century, however, the techniques of pumping water by windmills had already made such progress that, after being surrounded by a strong embankment, some of these lakes could be drained. The same techniques were applied to natural lakes: strong embankments were constructed, windmills were built, and the water was pumped out. Thus in the originally flat polder country a new type of polder occurred, the "droogmakerij," a lake that had been pumped dry. Many of these lake polders, of several thousand hectares each, are noted for the fertility of their calcareous clay bottoms. Others are underlain by physically and chemically less favorable peat soil. The origin of lake polders is shown in figure 2D, E, and F.

The evolution of the polder region has led to a very complicated system of boezems, polders, and drained lakes, in all of which the water levels can be controlled. Figure 3 shows the intricate pattern formed by these elements.

POLDER ADMINISTRATION

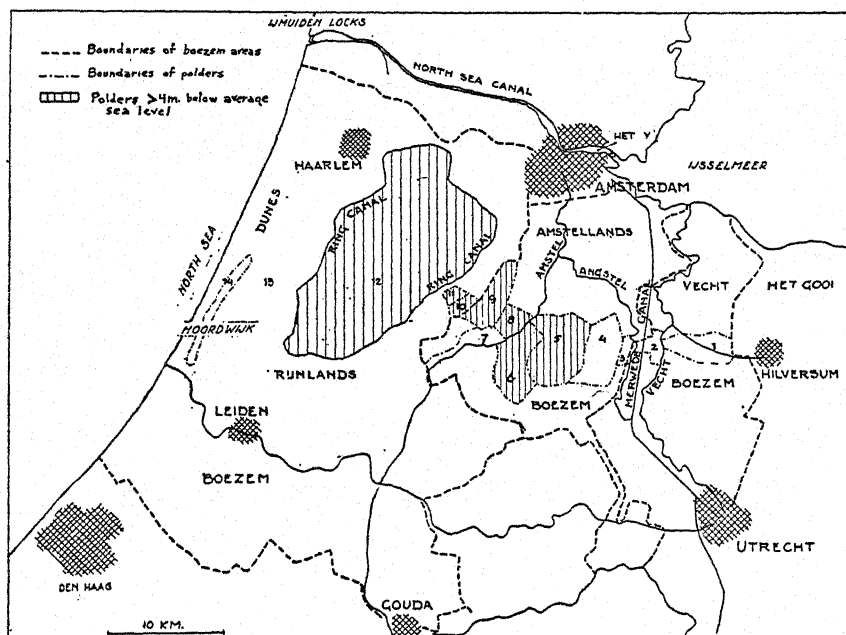
The settlement of people in the low-lying areas depends on embankments and sluices, canals and waterways, bridges, and pumping stations. Through necessity, all these water works came into being. It is no wonder that hydraulic engineering in the Netherlands has reached an extraordinarily high level. Water and human society are so closely related that the whole complex is denoted in Dutch by one word—"Waterstaat," a word without counterpart in other languages. The system of laws and regulations that governs the Waterstaat is based on the Constitution of the Netherlands. Elections of the polder boards, raising of polder taxes, and passing of resolutions take place in the polders in the same way as in Dutch municipalities. There is also a mandatory supervision of the observance of the resolutions and rules of the polder districts. Farmers play an important part on the boards of most polder districts.

WATER CONTROL IN BOEZEM AREAS

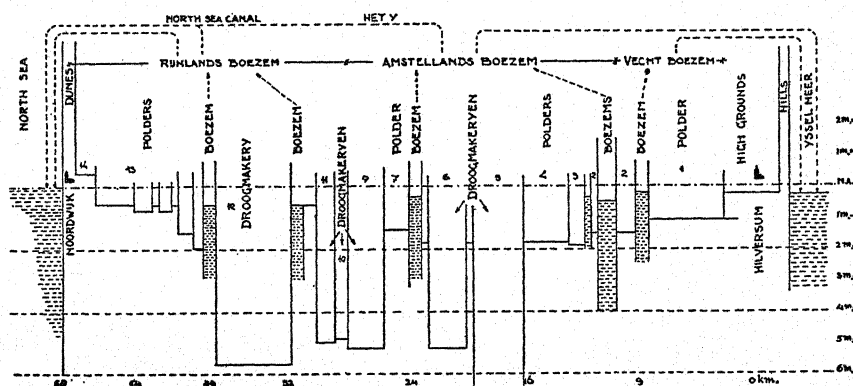
As an example of water control in a boezem area, let us consider the Rijnland boezem. Most of the areas shown in figure 3 belong to this boezem.

Rijnland covers 105,000 hectares, and its boezem waters have a surface of 3,700 hectares. In Rijnland, there are 216 polders. The boezem waters, consisting of former streams, lakes, and canals, provide drainage and serve for inland water traffic. The boezem is so regulated that its level can be maintained within very narrow limits at 60 cm. below average sea level.

Four powerful pumping stations along the borders of the boezem area take care of discharging the water pumped into the area by the 216 polders. During summer, water is let in from the main rivers to keep the boezem level constant and its water clean. In 1949, 650,000,000 cu. m. of water was discharged by pumping, and during the summer of that year, 300,000,000 cu. m. of water was let in. Special attention is given to the quality and to the salt content of the boezem water.



A. Map: 1. Kortenhoef polder, 2. Voorburgerpolder, 3. Donkervliet polder, 4. Vinkeveense polder, 5. Waterschap Groot Mijdrecht, 6. Mijdrechtse Droogmakerij, 7. Uithoornse polder, 8. Thamer binnenpolder, 9. Noorder Legmeerpolder, 10. Hornmeerpolder, 11. Stommeerpolder, 12. Haarlemmermeerpolder, 13. Boezem land with small polders, 14. Noordzijderpolder.



B. Profile showing polders, canals, and dikes between Hilversum and Noordwijk.

FIG. 3. DUTCH POLDER COUNTRY BETWEEN HILVERSUM AND NOORDWIJK

WATER CONTROL IN POLDERS

The water level

The low-lying and flat surface of the polder country has two important influences on the control of the water level: the low situation makes pumping necessary, and the flat surface requires an almost constant water level.

At first glance, it would seem that absence of a natural slope would severely hamper rapid discharge of water. On the other hand, the expert will realize immediately that a flow of water from high to low soils, where it would cause wet conditions, need not be considered.

A very important consequence of the horizontal surface is the equal depth of the water table below the surface of the land. This allows the water table to be kept at a level most suited to the requirements of the crops grown. This is an important feature of polder land.

The most notable application of this feature is in the growing of flower bulbs on excavated dune soils. In this area, described in more detail elsewhere in this issue, man has not hesitated to excavate the high sandy dune soils until the surface of the land was parallel with the water table and at a distance above it most favorable for bulb growing.

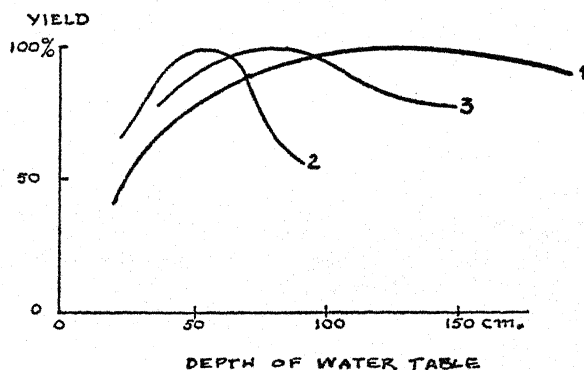


FIG. 4. RELATION BETWEEN CROP PRODUCTION AND GROUND-WATER LEVEL

1. Arable crops on clay soils. 2. Pasture on sandy soils. 3. Pasture on peaty soils. The curves are averaged over several years.

Ever since modern pumping techniques brought the maintenance of a constant water level within reach, the influence of this level upon crop production has been given attention. Studies revealed that the optimal level for maximum crop production depends on soil conditions as well as on the crops grown.

Soil with a low water-holding capacity, such as sand, requires a high water table, whereas young calcareous clay soils are most productive with low water tables. Shallow-root crops, like pasture and most vegetables, require a higher water table than do arable crops that tend to develop a much deeper root system. In peat soils, where danger of subsidence has to be taken into account, a high water table is required.

Figure 4 gives some examples of the relation between crop production and ground-water level. Observational data for these curves are being collected in rapidly increasing numbers.

In a polder with an entirely flat surface, made up of a single soil type, and with one form of land use, these curves can be used directly for determination of the required water level. These conditions, of course, are but seldom met. There will nearly always be differences in elevation, in soil type, and often in land use.

Then the water level must be kept at the height that will give maximum total crop production. The altitude of the surface, the distribution of the soil types, and the land use must be known, therefore, after which the optimal water level can be calculated from these data with the help of production curves for each case.

If the differences in elevation, soil type, or land use within one polder are too great, the polder is divided into separate parts, each with its own water level.

If the soil is of low permeability, as in many clay and peat soils, complications arise in maintaining good agreement between the water table and the water level in the polder. In that case the water table may be too high in winter and too low in summer, though the level of the polder water is kept constant. This discrepancy is illustrated in figure 5, showing these two levels for a grassland polder during 1946; the water table in summer falls far below the level in the polder ditches.² Under these circumstances many polder boards will keep the water in the ditches at a higher level during summer and somewhat lower in the wet season. The effect of this change in water level is often negligible, but in

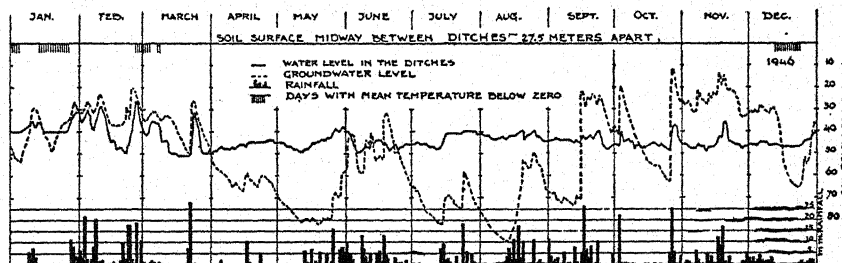


FIG. 5. WATER LEVEL IN THE DITCHES AND IN THE LAND BETWEEN THEM IN A GRASSLAND POLDER DURING 1946

many cases crop production can be raised by installing a system of tile drains to improve the flow of water between the land and the ditch. These tile drains will carry off excess water in winter, and if damage by drought is feared, they may be used for subsurface irrigation during dry periods.

Other activities besides crop production benefit from rigid control of the water level in the ditches. In most grassland polders the water-holding ditches replace fences. They also serve as watering places for cattle and in arable land as a source of water for sprays to control plant diseases. Sprinkling installations for vegetable crops grown under glass also withdraw water from the ditches. For several of these purposes, such as watering cattle and irrigating vegetables, the water in the ditches must be of high quality especially with regard to salt content.

Maintenance of the water level

During wet periods, the rainfall in the Netherlands, being of only moderate intensity, readily infiltrates into the soil and joins the ground water. Surface

² Dutch polder ditches are about 1-2½ m. wide and 1-1½ m. deep. In most grassland polders they are water-holding. In polders where arable farming is predominant the polder level is often so low that the ditches become dry in summer.

runoff occurs only if the structure of the topsoil is disturbed, as in the soils inundated by sea water during the war. In these soils, replacement of calcium by sodium in the exchange complex caused such deterioration of the structure that surface runoff resulted in some erosion, evidenced by gulleys along the borders of the parcels.

Normally, however, the precipitation joins the ground water and flows through the soil to the polder ditches. This flow is usually promoted by small field ditches or tile drains. The polder ditches carry the water to larger waterways or canals, from which it is pumped into the boezem by one or more pumping stations.

The high ground-water level in the polders and the flat surface of the land result in low water-storage capacity of the soil. The rainfall must be drained off quickly to prevent waterlogging. This requires a finely branched network of ditches and canals, which must be large enough to enable rapid flow from the parcels to the pumping station. The size of the waterways is especially important because the hydraulic head available for water transport is very small, in many instances no more than 1 or 2 decimeters over a distance of many kilometers.

As a consequence, innumerable ditches have been dug in reclaiming the low areas of the Netherlands. It is estimated that in the 1,000,000 hectares of low country 250,000 km. of ditches have been dug. In most grassland polders these ditches are still in existence, but in polders with arable land many of the smaller ditches have been replaced by tile drains, the main ditches left being 100–300 m. apart. New polders, like those being made in the Zuiderzee, have main ditches 250–300 m. apart.

The layout of a polder in its simplest form is illustrated in figure 6. The ditches in this rather recently reclaimed lake polder discharge into lateral or main canals, which carry the water to the pumping station. Halfway between these canals roads were constructed, with farms located along them. This regular pattern is found in polders made during the last four centuries. The layouts of former reclamations in the low country are more irregular. The course of roads and waterways in these polders depends largely on the outlines of the areas, which are often irregular. In the new Zuiderzee polders a compromise between the two systems is aimed at. In these, serious consideration is given to land-use planning.

The same water-carrying capacity per unit of surface is provided for all systems through which the precipitation must pass: field ditches or tiles, polder ditches, canals, and pumping stations. As already mentioned, rainfall during the wet season may be as high as 30 mm. a day. It is not necessary, however, to install pumping stations of this capacity, as no harm will be done by a too high level for a day or two. The experience of many centuries has shown that for the conditions in the Netherlands a water-carrying capacity of 8–12 mm. a day or 1.0–1.4 liters per second per hectare will be sufficient to avoid serious and prolonged rise of the water table above the level fixed. In determining the water-carrying capacity (per unit of surface) of a pumping station, the size of the area that must be served is given little consideration. Most of our polders are too small to allow a reduction for local showers. More attention is given to the region and its typical rainfall frequency.

Table 1 gives the daily precipitation, the amount of water pumped out, the level in the polder ditches, and the water table for a grassland polder during a period of rather heavy rainfall.

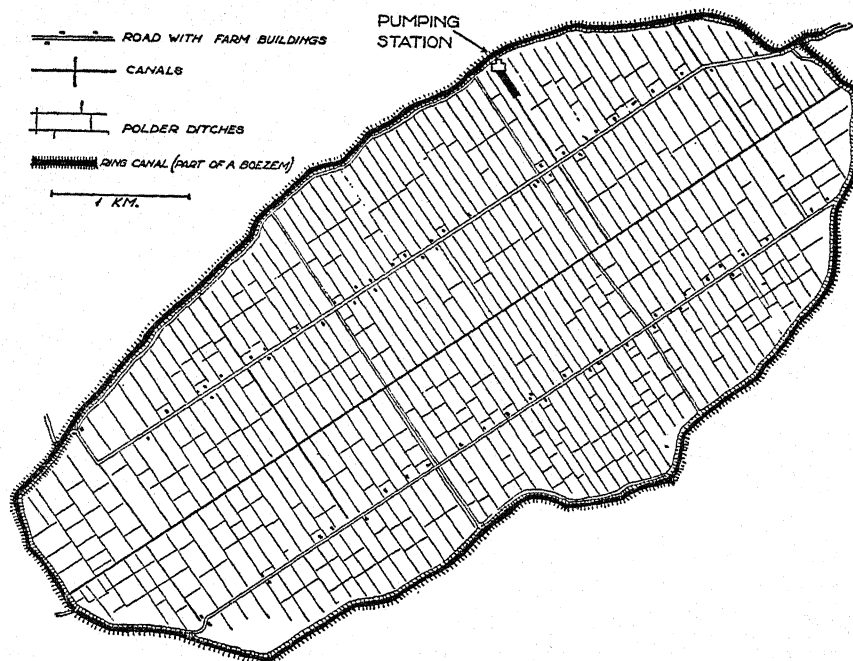


FIG. 6. MAP OF A RATHER RECENTLY RECLAIMED LAKE POLDER

TABLE 1

Precipitation, discharge of water, water levels in ditches and in land measured in a grassland polder during a period of rather heavy rainfall in December, 1949*

	DATE														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Precipitation.....mm.	0.2	0.0	3.5	26.5	1.4	7.0	1.3	0.5	19.0	2.3	0.6	0.0	0.3	0.3	0.0
Discharge of water...mm.	2.7	2.2	6.0	0.0†	9.4	9.4	9.4	9.4	9.4	9.2	0.0†	5.6	3.9	2.8	2.4
Water level in ditches‡...	57.5	—	—	—	33.0	—	—	57.0	—	—	—	56.5	—	—	71.5
Ground-water level‡.....	41.5	—	—	—	27.5	—	—	29.5	—	—	—	37.5	—	—	50.0

* Veendijk polder, Province of Utrecht.

† Generally no water is pumped out on Sundays.

‡ In centimeters below N.A.P. (a standard level, about as high as mean sea level). The altitude of the surface of the land is about 20 cm. below N.A.P.

As the polder levels are generally below the level of the boezem to which they belong, maintenance of these levels in summer is easy. As long as boezem water of good quality is available in sufficient quantities, water can be admitted from the boezem. The conditions mentioned are often the bottleneck of water control,

as the salt content of many boezem waters becomes too high in summer as a result of limited supplies of fresh water.

THE SALT MENACE

The sea with its salt water is a permanent menace to the part of the Netherlands close to it and lower than average sea level. Though the problem of keeping the water out has been almost entirely solved, the intrusion of salt is still a serious threat to Dutch agriculture. Salt water from the sea is gradually penetrating into the lower courses of the main rivers and has already reached inland 30 km.

Moreover, the shipping locks at the coast bring large quantities of salt water into the inland waters every time a ship passes through. The great locks of Ymuiden, connecting the port of Amsterdam with the North Sea and providing a passage for the largest ships, form the greatest entries for the salt. They pollute the inland waters with 2,300 tons of salt every time a ship is locked through.

Other, less obvious entries for the salt are formed by the Pleistocene sand layers in the subsoil, a formation about 200 m. thick in this area and highly permeable.

These sand layers are covered by relatively thin Holocene formations of clay and peat. As the polders, especially the lake polders, lie below mean sea level, the sea water has a tendency to seep through the Pleistocene subsoil toward the low polders and upward through the Holocene cover, a movement that is kept within bounds only by the low permeability of the Holocene layers. Without these layers, the lake polders would be uninhabitable.

Ever since this became known, experts have been anxious to prevent any penetration of the Holocene layers, though formerly many farmers sank deep wells into the Pleistocene sand to obtain for their own use the marsh gas that came up with the well water. These gas wells are still bringing much salt into the polder waters, but they are gradually being closed off.

The salt penetrating into the boezem and polder waters must be forced back again. Large quantities of fresh water are required for this purpose in summer. The main rivers, especially the Rhine, are the only sources available in this period. Large-scale use of their water is impossible. Not only would it facilitate penetration of salt from the sea into their lower courses, but their importance for navigation prevents withdrawal of much water during summer.

The only remedy for this situation would seem to be construction of storage basins from which water stored in winter may be used in summer. In general, a flat country like the Netherlands offers few possibilities for storing water, but the former Zuiderzee, now separated from the North Sea by a 30-km. dam, may play an important part in this respect.

A large part of this *IJsselmeer*, as it is now called, is being reclaimed, but after the reclamation works are finished, there will still be about 125,000 hectares of fresh water being fed by the river IJssel, one of the branches of the Rhine.

This lake has already done much to eliminate salt from the boezem waters of the northern provinces of Friesland and Noord-Holland. It is hoped that the IJsselmeer will be developed into a reservoir to meet all future demands for fresh water north of the main rivers. At present, the storage capacity of this lake is small, as the level is kept at very nearly the same height throughout the year.

FURTHER DEVELOPMENT OF WATER CONTROL

Large projects are now being planned to improve water control during the summer months. In many districts subsurface irrigation will eliminate the discrepancy between the ground-water level and the water level in the polder ditches and will increase crop production. This extension of subirrigation works, however, will make still higher demands on the quantities of fresh water needed. Agricultural and hydraulic experts are cooperating in a program of research set up on these subject.

The Dutch, having succeeded in making their low delta areas habitable by the discharge of water, are now aiming at the optimal use of the water available to them.

TILE DRAINAGE AND SUBIRRIGATION¹

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From the preceding paper in this issue it is clear that the topography and the climate of the Netherlands necessitate a permanent struggle to keep out water, on the one hand, and to supply water on the other. That paper deals with control in open waterways (main drainage); this paper deals with the corresponding tile drainage and with subirrigation.

The ground-water level of much of the Netherlands is high. In many regions it is at a depth of 0.5 m. in winter and of 1 to 1.5 m. in summer. A considerable part of the Netherlands, it must be remembered, is below sea level (fig. 1). In the higher sandy areas in the east the water table is several meters deep in many places, and in the loess soils of southern Limburg, more than 100 m. above sea level, it is more than 10 m. deep.

About 1845, mechanical tile-making in England paved the way for the application of tile drainage for land improvement on a large scale. In the Netherlands the first tiles were laid in 1852. Subirrigation was started much later, about the 1920's. Since then, the drained regions have been extended considerably (fig. 2). Subirrigation has made much slower progress.

A comparison of figure 2 with Edelman's new soil map of the Netherlands (5) shows that tile drainage has been applied almost exclusively to the heavier soils. Subirrigation, on the other hand, is used mainly on sandy soils, though peaty and even clayey soils (grassland) are now being subirrigated. Arable land, especially, is tile-drained; grassland, as well as some horticultural land, is subirrigated. This is because arable land is less subject to drought than is permanent grassland, though grassland should not be too wet in spring.

It follows that tile drainage and subirrigation are closely related and therefore can be best discussed together.³ Both aim to control the ground-water level, but in opposite directions (fig. 3). Tile drainage and systematic subirrigation are not necessary with open waterways (usually ditches 100 to 300 m. apart), provided the soil is sufficiently permeable to an adequate depth. For subirrigation, the level of the ditches should be raised to about 40 cm. below the surface. For good drainage, the water level should generally be lower than 1 m. Where the permeability of the soil is low, tile drainage or systematic subirrigation will be necessary. In the Netherlands, tile drainage, mole drainage, and trenching by means of shallow ditches are used, the last almost exclusively for subirrigation. In subirrigation, the level of the trenches and of the ditches into which the tiles or the

¹ The types of subirrigation discussed are known in the U. S. A. as *natural* subirrigation (by means of trenches) and *artificial* subirrigation (by means of lines of tile).

² Agricultural Experiment Station and Institute for Soil Research, Organization for Applied Natural Sciences.

³ Other methods applied sometimes, such as flooding and sprinkling irrigation, are not discussed here.

moles issue, is lowered in autumn, winter, and spring, so that the system can be used for drainage. This lowering of the level is also necessary sometimes in wet periods during summer to prevent excess water.

Tile drainage as well as subirrigation is controlled especially by the following factors: (a) surplus rainfall (drainage) or shortage of water (subirrigation), (b) optimum ground-water level in relation to the crop cultivated, (c) permeability of the soil and the depth at which this is a negligible factor.

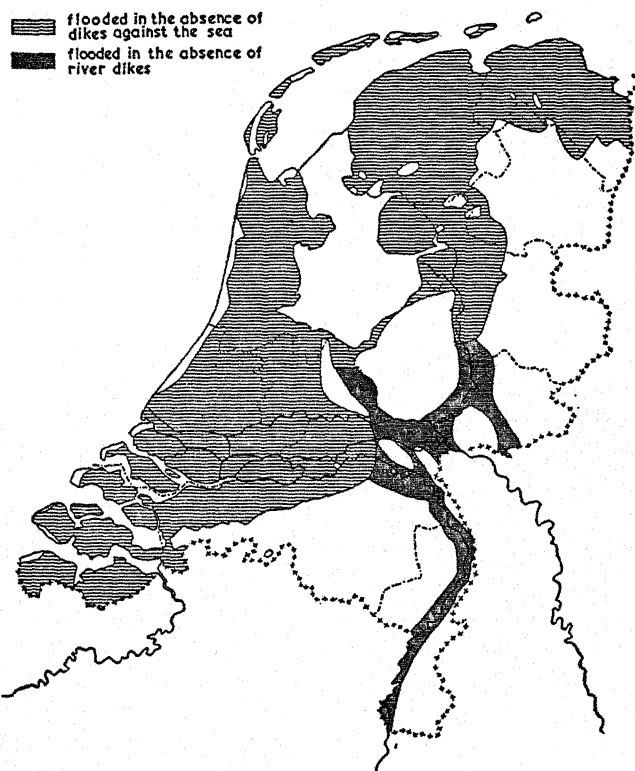


FIG. 1. REGIONS OF THE NETHERLANDS FLOODED IN ABSENCE OF DIKES

RELATION TO PRECIPITATION TO WATER CONTROL

In the Netherlands, rainfall, which is distributed rather regularly over the year, exceeds the sum of evaporation and transpiration. The difference, that is, the surplus rainfall, must be carried off, especially from November through February when evaporation and transpiration are both very low. The surplus rainfall is usually less than 5 mm. a day and scarcely ever more than 10 mm. Tile drainage is necessary when this quantity of water cannot be removed directly through the soil to the open waterways.

From May to August the sum of evaporation and transpiration exceeds the rainfall. The difference, 100 to 200 mm. depending on the rainfall, is withdrawn

from the soil by the crops. Crops may suffer from drought when the water-holding capacity of the soil is insufficient. This occurs in the Netherlands in the lighter soil profiles and at low ground-water levels. If these levels are high enough or can be kept so by means of subirrigation, no bad effects from drought are experienced. In this case a sufficient amount of water is supplied to the crops by capillary rise

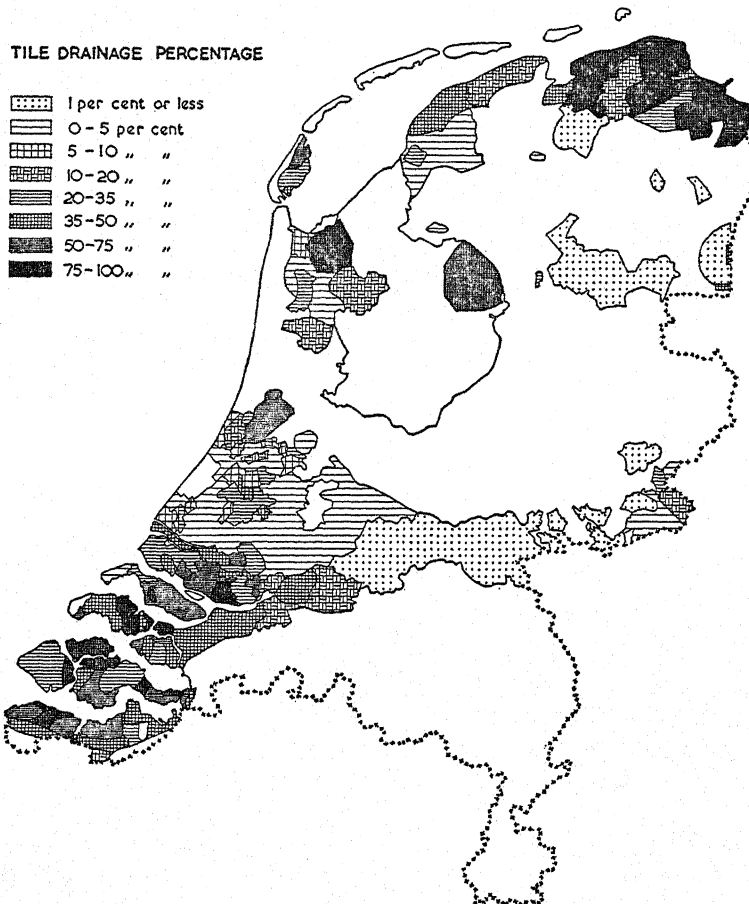


FIG. 2. REGIONS OF THE NETHERLANDS WITH TILE DRAINAGE AND PERCENTAGES OF THE SOILS DRAINED

from the ground-water level. The water supply needed for subirrigation may be estimated at 4 mm. a day for about 100 days, from the middle of May until the end of August.

Without subirrigation, water is withdrawn from the soil in summer. With decreasing evaporation and transpiration in autumn, this water must be replaced before surplus rainfall occurs. The tiles begin to carry off water generally late in autumn.

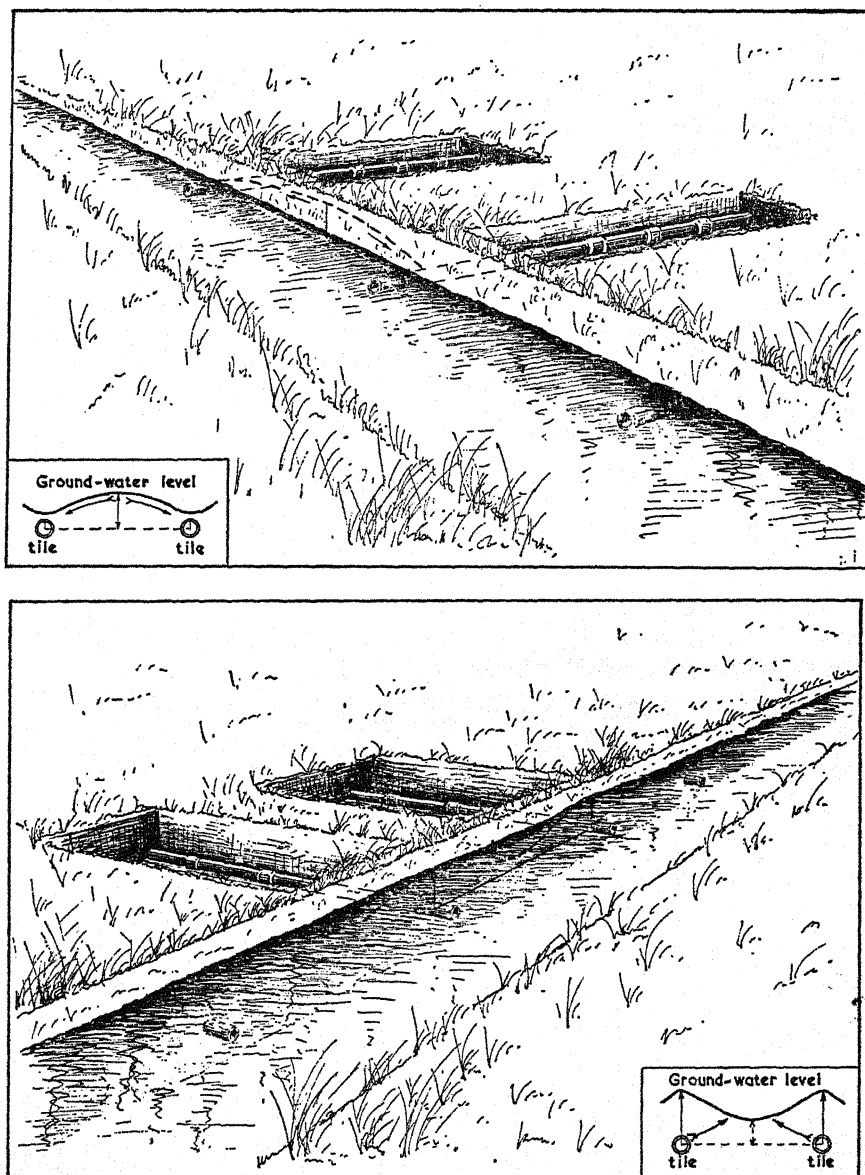


FIG. 3. SCHEMES OF TILE DRAINAGE (TOP) AND OF SUBIRRIGATION (BOTTOM)

In view of the mutual relation of the two systems, the lines of tile are supposed to discharge below the water level.

RELATION BETWEEN GROUND-WATER LEVEL AND CROP YIELD

The primary purpose of drainage is to prevent too high ground-water levels in winter and spring, and that of subirrigation is to keep these levels sufficiently high in summer. The presence of adequate moisture in the soil layers containing

crop roots and, at the same time, sufficient aeration of the soil are important plant-growth needs which, in the Netherlands, are best met by control of the ground-water level.

To determine the optimum ground-water level is a complicated problem, for one has to cope with normal variations in the level during the year—high in winter, decreasing in spring and summer, rising again in autumn—and also with the influence of temporary periods of rain and drought. Moreover, the effect of the ground-water level may vary for different crops, such as winter and spring cereals and root crops.

The problem can be solved by two methods: (a) by providing, in the soil of an experimental field, different ground-water levels that are constant during longer or shorter periods; (b) by determining statistically by measurements on many fields under different conditions the effect of the ground-water level on crop yield (6). In this case the average ground-water level in a certain part of the growth period is usually correlated with the yield, the variation of this level being taken into account.

To give some idea of what is known about this problem, the year is divided into two parts, namely, summer, or the actual growing period, and the rest of the year.

Generally, a low ground-water level in autumn, winter, and spring will have no detrimental effect on soils and crops. This does not hold for some peaty soils which show shrinking or irreversible drying at too low ground-water levels. Moreover, on some soils it may be useful to store water for the crop in summer by maintaining the highest justified level in winter.

About 70 years ago drainage in the Netherlands left much to be desired. A high ground-water level used to occur in autumn, winter, and spring, and many soils contained excess water, leading to poor structure, especially of clay soils. This is no longer generally true, as soil structure has greatly improved. Common practice now is to keep ground-water levels of clay soils as low as possible.

It remains to be seen, however, whether a high water level, especially in winter, affects later crop growth if the level does not rise into the topsoil. Investigations on a water-level trial field, which are discussed later, have shown that the crop yield obtained at a ground-water level kept at 40 cm. below the surface from November to March and followed by a decrease to 120 cm. below the surface was not significantly lower than the yield obtained at a water level kept at 120 cm. below the surface during the whole year. A similar result was obtained in the Northeastern Polder, an enclosed Zuiderzee polder. Admittedly, information on the maximum water level allowable during winter is still inadequate. The general recommendation is that drainage is adequate if 5 mm. of surplus rainfall can be carried off without raising the ground-water level higher than 50 cm. below the surface.

The foregoing comments apply not only to arable land but generally also to grassland, which requires less drainage. Grassland in the Netherlands, therefore, is usually not tile-drained.

Obviously, in spring a lowering of the ground-water level is advisable in view

of the increasing root development of the crops. In summer the most desirable water level depends more on soil condition and profile.

For arable land important data have been obtained on a ground-water level trial field on heavy clay soil at Nieuw-Beerta (11). This field has been divided into five strips, 86 by 25 m., on each of which the ground-water level can be kept constant, within a few centimeters, to a different depth (40, 60, 90, 120, and 150 cm.). This is attained by means of tile drains only 2 m. apart that discharge below water level into deep sewers in which the desired water levels are maintained by small weirs. This is accomplished by drainage in winter and by subirrigation in summer. On three plots crossing the five strips three different crops are grown annually in the usual crop rotation.

During the first 7 years the ground-water levels were kept constant all year at the five depths mentioned. In the first 5 years no differences were noted in tillability and structure of the soil. After this, the 40-cm. strip and, to a lesser degree, the 60-cm. strip showed a more compact and sticky topsoil. On the other three strips the structure had not deteriorated. On all strips, germination and growth of winter and spring crops were the same until a certain time, usually late in spring, when differences were noted especially with cereals and peas. On the 40- and 60-cm. strips, the crops yellowed. Later, those on the 90-cm. strip were similarly affected. On the 120- and 150-cm. strips, normal, healthy color was maintained. On the strips with the highest ground-water levels, the crops ripened sooner and the yield was lower. The cause of yellowing and decrease in yield is partly nitrogen deficiency. With increasing depth of the water level, the increase in yield was great at first but later became smaller.

Other crops, like beans, rape seed, and caraway seed, showed less yellowing or none, but usually the yield was higher at the lower water levels.

During the last few years the ground-water level on the 60-, 90-, and 120-cm. strips has been kept at 40 cm. from November to March and at 60-, 90-, and 120-cm. for the rest of the year. For the most part, growth and yield of the crops appear to have been unchanged by this measure. The higher water level during winter, therefore, proved not to have been injurious. This experiment is being continued to determine whether the soil structure will eventually be affected by this treatment.

Table 1 shows the yields of winter wheat on this field. The maximum yield has not yet been reached.

At an insufficient water-holding capacity, an optimum ground-water level occurs. A case in point on sandy loam was placed at the author's disposal by W. C. Visser. The statistical method was used, taking into account many plots on this soil type showing a great variation of ground-water level. Figure 4 shows experimental results of the effect of different water levels on the yield of potatoes.

In most Netherlands soils, the water level in spring is too deep to fit the rising curve (fig. 4) for decreasing water levels. Another case is dealt with in table 2. This is concerned with oats on sandy soils having an upper layer rich in humus of different thickness underlain by sandy subsoil of varying degrees of fineness, expressed by *U*-number, or specific surface. The thickness of the humus layer

TABLE 1
Effect of ground-water level on yield of winter wheat
Grain and straw in kgm. per 100 sq. m.

	DEPTH OF GROUND-WATER LEVEL (CM.)									
	Grain					Straw				
	40	60	90	120	150	40	60	90	120	150
1947-48*	19.8	27.3	31.9	36.5	41.9	43.1	53.1	60.8	70.6	78.2
1949-50†	31.3	37.6	42.5	45.8	51.3	57.5	64.3	73.8	76.5	89.9

* Ground-water level constant throughout the year.

† Ground-water level on the 60-, 90-, and 120-cm. strips, 40 cm. from November to March; at original depths for the rest of the year. Other strips kept at original depths all year.

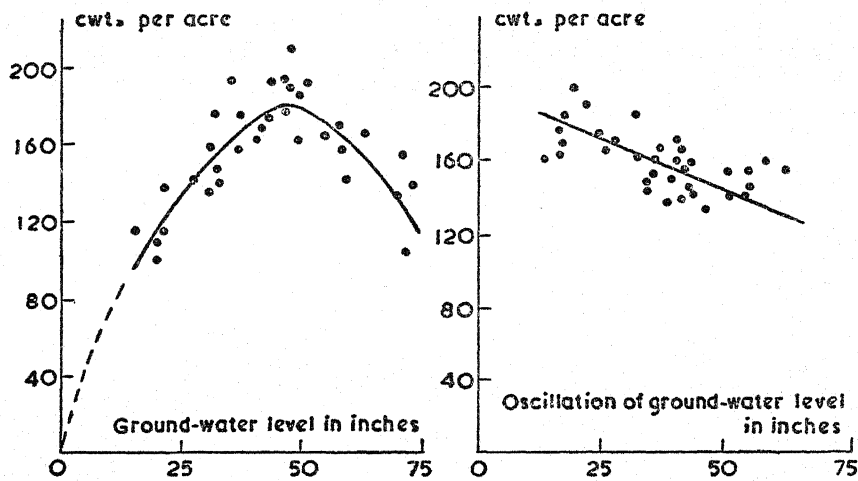


FIG. 4. RELATION OF YIELD OF POTATOES TO DEPTH OF THE GROUND-WATER LEVEL (LEFT) AND TO OSCILLATION OF THE LEVEL (RIGHT)

TABLE 2
Effect of thickness of sandy humus layer and of specific surface of sandy subsoil on optimum ground-water level of arable land

SPECIFIC SURFACE (U) OF SANDY SUBSOIL	DEPTH OF WATER LEVEL			
	Humus layer 20-40 cm.	Humus layer 41-60 cm.	Humus layer 61-80 cm.	Humus layer 81-100 cm.
	cm.	cm.	cm.	cm.
40-70	90	110	130	150
71-80	100	120	140	160
81-100	110	130	150	170

and the fineness of the sand are the factors dealt with statistically. Table 2 shows the water levels at which the depression in yield caused by water shortage does not exceed 10 per cent. The ground-water level at which this depression occurs

is lower the thicker the humus layer and the greater the *U*-number of the underlying sand, that is, the finer the sand.

Permanent grassland probably does not show a maximum water level, but only an optimum for all soil profiles, even those of the heaviest clay. According to 't Hart (7), growth of grass of varying productivity in 3 years under different weather conditions and on clay, peaty, and sandy soils, reached a peak in May. This was followed in all cases by a decrease. In the latter part of summer, growth again increased. Productivity in summer appeared to be relatively low. To support as many cattle as possible and to increase their milk production, it is desir-

TABLE 3
Effect of subirrigation on yields per hectare of grassland and of arable land

	SUBIRRIGATED	NOT SUBIRRIGATED
Grassland		
Hay (two cuttings) kgm.	7,100	3,900
Grazing days	1,110	780
Arable land		
Winter wheat (grain) kgm.	3,920	3,630
Rye (grain) kgm.	3,525	3,510
Spring wheat (grain) kgm.	2,820	2,275
Spring barley (grain) kgm.	3,095	2,740
Mangolds (roots) kgm.	87,700	81,600
Potatoes (tubers) kgm.	35,900	35,800

TABLE 4
Effect of thickness of sandy humus layer and of specific surface of sandy subsoil on optimum ground-water level of grassland

SPECIFIC SURFACE (<i>U</i>) OF SANDY SUBSOIL	DEPTH OF WATER LEVEL		
	Humus layer 20-30 cm.	Humus layer 31-40 cm.	Humus layer 41-60 cm.
	cm.	cm.	cm.
40-60	85	100	100
61-75	100	115	115
76-90	100	115	115

able to increase the yield of grass, especially in summer. For this purpose more water must be made available, though the decrease in grass yield is due to other factors also. Additional water is generally supplied by subirrigation, the necessity for which increases as the water-holding capacity of the soil decreases.

The influence of subirrigation on yields of grassland and of cultivated crops is shown in table 3.

Table 4 shows the effect on optimum ground-water level of permanent grassland on sandy soil with humus layers of varying thickness and with underlying sand of different degrees of fineness. The table indicates the water levels at which decrease in yield will be not more than 10 per cent below the maximum.

That permanent grassland on a sufficiently permeable clay soil also may suffer from drought in dry periods when the ground-water level is 1 or more m. below the surface has been demonstrated. In this case subirrigation was by mole channels (7 cm. in diameter) 50 cm. below the surface discharging below the ditch-water level. The ground-water level on the subirrigated part was 40 to 45 cm., on the nonsubirrigated one more than 1 m. The great differences in yield are shown in table 5; rainfall in June, July, and August had been below average.

Serious drying out of grass on these soils is due to the so-called "nut" structure in the layer 15 to 40 cm. below the surface. This adversely affects deep root development and prevents capillary rise of water from deeper layers.

On clay soils of otherwise excellent quality, damage may result from heavy fertilization and intensive use of grassland, leading to trouble from drought, stagnation, or at least decreasing growth. When production is very high (10,000 kgm. of milk per hectare), this sort of clay soil shows an optimum ground-water level, which does not occur with a normal yield of 5,000 kgm of milk. These soils, therefore, have a maximum water level for normal yields.

TABLE 5
Effect of subirrigation on yield per hectare of grassland on clayey soil

DATE OF MOWING	YIELD OF FRESH GRASS	
	Subirrigated	Not subirrigated
	kgm.	kgm.
August 5	15,600	1,800
September 10	18,600	3,600
November 11	10,800	6,300

Apparently, then, the ground-water level, which depends on the soil profile and the ditch-water level, should be raised during the growing season. The optimum ground-water level, the ditch-water level, and the quantity of water required daily (about 4 mm. on grassland in dry periods and probably somewhat less for arable crops) are the fundamental data for calculating the necessary distance of the subirrigation tiles and trenches.

RELATION OF SOIL PERMEABILITY TO WATER CONTROL

If the required conditions for tile drainage or subirrigation are known, the distances between the lines of tile can be calculated, provided some other factors also are known. The problem has been reduced to the water flow in the soil (2, 3, 10).

The other factors that must be known are the permeability of the soil and the depth to which the soil retains this permeability. In soils that are homogeneously and isotropically permeable to a great depth, the intensity of flow to deeper layers decreases. Calculations have shown that the permeability of the soil is of no importance at a depth exceeding one fourth the distance between the tiles or the ditches in the drainage or subirrigation systems, since the flow from or to

these systems at this depth is negligible. For example, if the tile drains are 10 m. apart, soil permeability at a depth of more than 2.5 m. below the tiles can be disregarded; if there is an impermeable layer nearer to the surface, the position of this layer must be determined.

If the impermeable layer is relatively close to the surface in comparison with the distance between tiles and ditches, the product of the permeability coefficient and the thickness of the permeable layer indicates the "conductivity for water" of the soil. In cases of equal permeability, this conductivity decreases as the level of the impermeable layer rises in the profile and the required distance between the tile drains consequently decreases at the same rate.

The calculations become more difficult if the soil, because of differences in the permeability of the profile, is not homogeneously permeable. Nevertheless they can be made.

It follows that it is important, for determining drainage as well as subirrigation, to know the permeability of the soil, the rate at which it changes in relation to depth, and the depth at which it may be disregarded.

Apart from sandy soils with a 16 μ fraction not exceeding 5 per cent, there are no methods for determining the permeability coefficient of the whole soil profile. Consequently, it is not yet possible to calculate the exact drainage distance required for other soils. There is a field method for determining the permeability to a depth of 2.5 m. below the surface, that is, to about 1.5 m. below tile drains set at a depth of 1 m. Nothing is known about permeability at a greater depth, although the kind of soil may provide some clue.

If the permeability is low and consequently the distance between the lines of tile is small, it may be safely assumed in computing the drainage distance that the soil retains the same permeability to a depth equal to one fourth this distance. If the permeability is high, this assumption is not valid because of the compression by overlying layers. In this case it is supposed that the soil retains its permeability to a somewhat greater depth than that to which permeability has been determined (rounded off to $\frac{1}{4}$ m.). Below this level, the soil is supposed to be impermeable. If the drainage distance is based upon this supposition, and if the soil actually is impermeable to the assumed depth, a condition rarely found in the Netherlands, the distance will be correct. If the soil remains permeable to a greater depth, the computed drainage distance is too small and consequently is safe. The computed distance figure is rounded off upward. To-day, drain distances are indicated satisfactorily by this method.

DETERMINATION OF SOIL PERMEABILITY

The definition of 'permeability' is based on Darcy's law, in which the permeability coefficient represents a layer of water at a definite temperature flowing per unit of time through a section in the soil perpendicular to the direction of flow, if the hydraulic gradient is equal to 1. At a definite ground-water temperature, and consequently at a definite viscosity of the water, this law can be expressed by the following formula:

$$V = \frac{Q}{F} = K \frac{\Delta p}{l} = KI$$

in which Q represents the quantity of water per unit of time flowing through a column of soil of length l (in the direction of the current) and cross section F , if the difference in pressure of the water at both sides of the column is equal to Δp . I gives the hydraulic gradient and V the quantity of water flowing through the column. If this difference in pressure, Δp , is expressed in a column of pure water, I has no dimension. The permeability coefficient K is equal to V if $I = 1$. According to this definition, the permeability coefficient has the dimension of lt^{-1} . Usually this is expressed in meters per 24 hours.

For structureless sandy soils this determination is based on a direct application of Darcy's law, whereby all factors will be determined or are known and consequently K can be computed (8). If the soil in a natural situation has a pore volume different from that during the determination and if the ground water has a different temperature, then the individual factor must be adjusted accordingly. This determination of permeability has but little significance for computing the distance between the lines of tile, since sandy soils rarely require systematic drainage. The distances between tiles or moles of the subirrigation system are usually determined by means of experimental fields.

In other soils the permeability of which is determined by cracks and by root and worm holes instead of by pore spaces between the soil particles, the auger-hole method is used. In a vertical auger hole extending below the ground-water level, the velocity at which the water rises after the hole has been drained depends upon the permeability of the soil. If the relation of the velocity of rise, the permeability coefficient, and the other factors influencing this velocity is known, the permeability coefficient can be computed.

This method determines only the permeability of the soil below the ground-water level. In the main, it determines the permeability of the layer between the water level in the hole, that is, ground-water level, and the bottom of the hole. The radius of the column of soil around the auger hole, the permeability of which is measured, is relatively small, about 0.5 m.

The auger-hole method, originated by Diserens (4), was improved by the author (9, 10) and by Kirkham (12), Van Bavel (1), and Ernst.

As this method measures the permeability of only a small column of soil, it is necessary to repeat the determination on several spots, preferably five or six per hectare, unless large areas are under investigation. To determine the changes in permeability in relation to depth below surface level at these spots, holes of different depths at distances of 1 to 2 m. are bored on every plot.

The permeability varies from 0.1 m. per 24 hours in the finer sands to more than 30 m. in the coarse river sands. That of peaty soils ranges from 0.01 to more than 10 m. Phragmites peat is sufficiently permeable; sphagnum and carex peats are often much less permeable. In Dutch clay soils the variation is from 0.01 m. to more than 30 m. per 24 hours. Some clay soils have a better permeability than coarse sandy soils.

DETERMINATION OF LAYOUT OF DRAINAGE AND SUBIRRIGATION SYSTEMS

For systematic drainage, the drainage distance, in practice, is often based on results with similar soils. Sometimes special experimental fields are laid out. This

is necessary if the soil before being drained has a high moisture content and is seriously desiccated by drainage and cultivation and if the permeability increases as a result of cracking, as in newly reclaimed clay soils. Sometimes the permeability varies so much from spot to spot that no average permeability coefficient can be determined, as in very young heavy marine clay soils. Drainage recommendations are being based more and more commonly and with satisfactory results on permeability determinations. The minimum applied drainage distance is about 7 m. The maximum distance is defined by the distance between the ditches. In this connection, a plot is not drained if the required drainage distance exceeds half the distance between the ditches.

When special experimental fields are used to determine distances for the sub-irrigation systems, the required ditch and ground-water levels as well as the most practical means of execution are deduced from the results.

PRACTICAL OPERATION OF TILE DRAINAGE AND SUBIRRIGATION

Drainage

Systematic drainage was formerly executed by means of trenches. Nowadays, tile drains are most common, though sometimes moles are used. The advantages of tile and mole drainage over trenching are easier cultivation of the land, no loss of land, and less weed development. Trenching is sometimes practiced for a few years when the soil is very wet, is low in permeability, and is insufficiently cleared of salt, as in newly reclaimed heavy clay soil. In time, the drains may become inactive or blocked. Tile drainage is then applied as soon as the soil is sufficiently dried and cleared of salt.

Since the regions needing systematic drainage are intersected by ditches, simple drainage is usually applied rather than compound drainage, that is, primary and secondary lines of tile. In simple drainage, each row of tile discharges directly into a ditch. The advantage of this system is that the efficacy of each tile line can easily be verified. Moreover, the construction is simple. When lines of tile become inactive, they can easily be cleared by passing through them poles on which rubber disks have been fixed, followed by washing.

Unglazed brick tile 30 cm. long and with an inner diameter of 5 cm. and an outer diameter of 7 cm. are used. The drainage distance generally does not exceed 30 m. Only in compound drainage systems does the diameter vary according to the amount of water to be discharged.

The drain tile are sometimes flanged. Although more expensive than tile without flanges, they can be joined more securely. They are used especially in soft soils, such as peaty or clay soils with soft layers at drainage depth, if there is risk of local displacements due to unequal settling of the profile.

The lines of tile are generally 100 to 150 m. long. They may be laid horizontally and discharge below the water level in the ditches, though usually they slope about 10 to 20 cm. per 100 m. and discharge above the water level. The sloping tile lines do not become blocked so quickly as the horizontal ones, for the silt accumulation cracks during summer and is more readily removed by subsequent water flow. Moreover, the sloping lines are more easily laid. Their nearness to the surface is a drawback only where ditch-water levels are high.

The depth of the tile lines is determined by the ditch-water level during winter. This depth varies from 80 to 150 cm. below the surface.

Few data on the length of period of performance are available. In some places the tile lines function satisfactorily for more than 50 years. In other places, they become blocked after 1 or 2 years and have to be cleared. It is assumed that well-laid tile continue to function for 25 years on an average.

The lines of tile usually are laid in trenches dug by hand. In the reclaimed polders of the former Zuiderzee, mechanical excavation is practiced. After the bottoms of the ridges have been given the correct slope, the tile are laid. To prevent soil particles from penetrating into the tile, a thin layer of filtering material is sometimes deposited on the tile or around them. Frequently, coarse peat dust is used. On this, a thin layer of topsoil is deposited. Then the ridge is filled with the original soil. To maintain the permeability of the soil in the ridge, especially where permeability is low, lime is commonly applied during the filling if the pH is low.

Subirrigation

For systematic subirrigation of grassland, trenching to a depth of 60 to 80 cm. is most common, although use of lines of tile or mole channels is increasing, especially in peaty and clay soils. For horticultural use, subirrigation with tile is most common, especially on sandy soils. In clay and peaty soils, mole channels are more commonly used for subirrigation than for systematic drainage. This is because shallow mole channels are more satisfactory for subirrigation than for drainage. Moreover, mole channeling is much cheaper than tiling even if new channels have to be made every 2 years.

The depth of the tile lines or channels, 40 to 60 cm., for systematic subirrigation is less than that for drainage. The lines of tile or mole channels are always horizontal and discharge below the water level in the ditch.

In the Netherlands, considerable variation in the weather affects the time at which subirrigation in spring should be started. During hot, dry spells in summer, a ground-water level that will be too high during subsequent wet spells may be desirable. A high ground-water level in clay soils during the whole period of subirrigation is not desirable (11). It seems preferable to moisten these soils by a high ground-water level for short periods, followed by periods of low ground-water level.

In special cases, it is possible to subirrigate by raising to a sufficient height the water level of brooks in elevated, slightly sloping, but comparatively flat, sandy land. If the water level of the brook is raised early in spring, the winter water is stored and produces a higher ground-water level. The result of this rise will be better if the water level of the ditches is raised at the contour lines. These ditches discharge water into the brook at some distance upstream from the weirs. The effectiveness of this measure has been determined both by experiments and by calculations based on the permeability of the soil profile down to the impervious layer and by other tests.

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RECLAMATION OF HEATHLAND AND ITS CULTIVATION

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More than half the soils of the Netherlands consist of peat and sand, which are naturally infertile. Another article in this issue deals with the reclamation of peat soils. The farmland on sandy soils has been acquired by reclamation of forest and heath.

Reclamation of heath was impossible before the introduction of chemical fertilizers. Though no reliable statistics are available on the extent of heath reclamation, it is safe to say that during the last 120 years the area of heathland has decreased by about 500,000 hectares. Only about 100,000 hectares of heathland remain in the Netherlands. Reclamation of this land is virtually at an end, as the small areas left must be reserved for scientific, recreational, or military use.

In general, the heaths are classified as high, medium-high, and low heathlands.

PEDOLOGY, VEGETATION, AND MOISTURE RELATIONS

High heathland

The soils of the high heathlands are strongly podzolized. Below the heather sod, which, as a rule, is 5 to 8 cm. thick, lies a layer of bleached sand (A horizon) of varying thickness. This is underlain by an iron-humus pan (B horizon), which is usually only about 10 cm. thick, rather poorly developed, not very hard, and of a mottled brown. In many places it is an iron pan with a low humus content; in other places, however, a humus pan occurs together with an iron pan. This B layer is better developed, thicker, and more reddish in the coarser sandy soils than in the fine sands. Below the pan lies the original sand (C horizon).

The vegetation usually consists of a poor growth of *Calluna vulgaris* with scattered *Juniperus communis* and *Pinus sylvestris*.

In winter the water table may occasionally rise to within 80 cm. of the surface, but generally the highest water levels lie at a far greater depth. In summer, the ground-water level will fall to a depth of several meters.

The water relations of these soils are very poor, not only because of the low water table, but also because of the very poor moisture-holding capacity of the topsoil. The crops grown on these soils after reclamation often suffer from lack of moisture.

Medium-high heathland

The soils of the medium-high heathlands are less strongly podzolized than those of the high heathlands. The sod of the heather growth is 8 to 12 cm. thick and generally is stiff and tough. It is underlain by a layer of bleached sand, which, in turn, is underlain by a thoroughly developed iron-humus pan, normally 20 to 25 cm. thick. This pan is reddish brown and very hard. In profiles lying on slopes, it is cemented.

¹ Dutch Heath Reclamation Company.

The surface is covered with a dense growth of *Calluna vulgaris* together with some *Erica tetralix* and a little gray *Corynephorus canescens*.

The highest water levels in winter are only about 50 cm. below the surface; in summer the water table falls markedly.

The water relations of these soils are not very good. Although the water-holding capacity of the topsoil is better than that of the high heathlands, the topsoil is rather thin, and for this reason its moisture content is quickly exhausted. In spring the crops can draw from the subterranean water, which is still at a rather high level. In summer, this is no longer possible, because the water table has fallen too far, and late-growing crops like mangolds may suffer from lack of moisture.

Low heathland

The soils of the low heathlands have a rather thick, humus-rich sod, which may change into a peaty sod, about 15 cm. thick. Underlying the sod is a layer of sand with a high percentage of organic material. In this layer small quantities of bleached sand sometimes occur as a result of podzolization during periods in which the water table is low. The humic sand layer is underlain by a poorly developed soft brown iron-humus pan. Below the pan lies the unaltered sandy subsoil, which contains spots of glei and which soon gives way to bleached reduced sand.

In many places the sand lying immediately under the sod contains root channels. The organic material in this sand may have been derived from the various kinds of grasses that comprise a large part of the vegetation. *Calluna* is entirely absent, but *Erica* is found in many places, together with common grass, *Corynephorus canescens*, *Salix repens*, *Myrica gale*, and *Drosera*.

In winter, the water tables in these profiles are so high that the soils are either soggy or flooded. In some cases the summer water table may fall to a depth of several meters; in others, it falls to only 60 to 80 cm. below the surface. These differences have a great influence on the quality of the sod. In spring, as the water level falls, peat begins to form. In summer, if the water level becomes too low, this new formation of peat, called "gliede," dries out and is destroyed. If the water does not fall below 60 to 80 cm., the environment will remain sufficiently moist to permit continued growth of the peat deposit during the summer. This peat, of course, is found in the lowest spots.

The water relations of these soils are rather good. The humic topsoil is fairly thick, and water can be drawn from the subsoil during a good part of the growing season. Symptoms of desiccation, such as occur on reclaimed high heathlands and to a somewhat less degree on reclaimed medium-high heathlands, are absent here. Sometimes excess moisture may be found locally, but this is taken into account in land use, as these soils are generally put under grass.

AGRICULTURAL POSSIBILITIES

High heathland

Reclaimed soils of the high heathlands should be put into forest. In that case, the cost of reclaiming would be low because extensive leveling is unnecessary.

Because of the shortage of land, however, high heathland is also cultivated. The results are not particularly good, because of the lack of moisture. Rye is virtually the only grain crop that can be grown, and it produces only about 1,500 to 1,700 kgm. per hectare.

Medium-high heathland

After reclamation, medium-high heathland can be cultivated. Though the higher areas are too dry, the lower areas can be transformed into sandy arable land of moderate quality if adequate supplies of organic matter are provided regularly.

The principal crops on such soils are rye and potatoes, but mangolds also are grown. The yield of rye here is 2,200 to 2,500 kgm. per hectare; that of potatoes, about 15,000 kgm.; and that of mangolds, 25,000 kgm. Though the lowest areas may be devoted to grassland, use of these soils for permanent pastures is not recommended.

Low heathland

In reclaiming the low heathland soils, it is necessary to take into account their various elevations. These soils are suitable for cultivated crops and for grassland. The lowest areas must be used for pasture, because they are too wet for arable land. Cultivated crops would require better drainage, but this would lower the water table in the surrounding higher areas and consequently would reduce the value of the higher land.

The higher areas of the low heathlands are well suited to cultivation. Mangolds yield especially well, and potatoes and rye produce better crops than do the soils of the high and medium-high heathlands. Rye yields 3,000 to 3,200 kgm. per hectare; potatoes, 30,000 to 32,000 kgm.; and mangolds, about 80,000 kgm.

RECLAMATION REQUIREMENTS

In the reclamation of heathland, the following principles must be considered:

The sod must be left in the upper part of the profile to enrich the topsoil with organic matter and to prevent anaerobic decomposition.

The bleached sand, from which all plant nutrients have been leached out, should be removed to as great a depth as possible.

Impermeable layers must be broken up to a depth of at least 0.8 m.

A layer of good sand, about 0.2 m. thick, must be spread over the loosened sod. As a rule, the iron-humus layer of the original profile will serve the purpose.

To save expense, leveling operations must be kept to a minimum. They must be carried out in the subsoil so that the desired soil remains on top.

Formation of large holes in the spaded soil must be avoided. For this reason, it will often be necessary to burn the vegetation of the heathland that is to be reclaimed, though this involves a loss of organic matter.

RECLAMATION METHODS

Both mechanical power and manual labor are used in reclaiming heathland. In mechanical reclamation, the plow plays the most prominent part. In the beginning of large-scale reclamation, when flat grounds with fairly regular profiles

were treated, the tractive power was supplied by oxen (fig. 1). Later the oxen were replaced by horses. Still later, vast areas were reclaimed by the steam plow,



FIG. 1. PLOWING HEATHLAND WITH OXEN

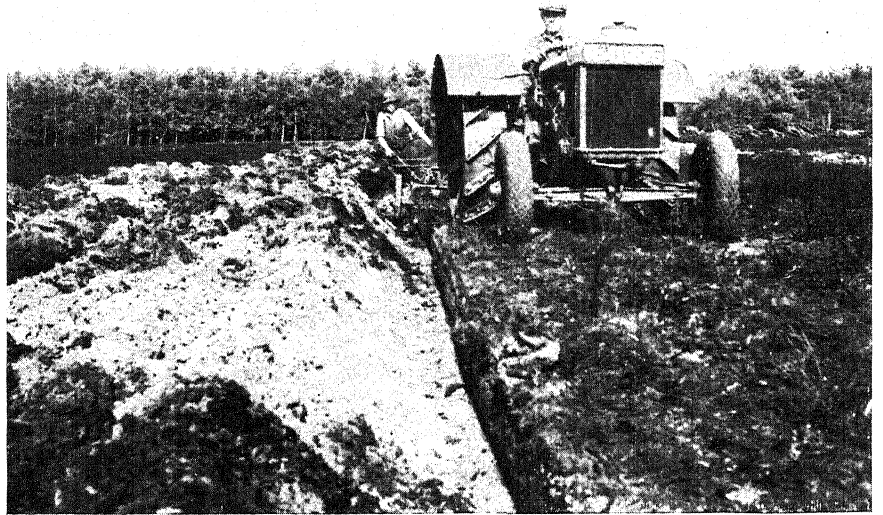


FIG. 2. PLOWING HEATHLAND WITH A TRACTOR

which was attached to a long steel cable and drawn to and fro by two portable engines, one on each side of the plot to be reclaimed.

Nowadays, only tractors are used (fig. 2). On flat land without an iron-humus

pan, the only operation required is to plow the soil to a depth depending on the desired position of the sod in the profile.

If there are impermeable layers, a plow with a subsoil trencher must be used. The plow turns the soil to the depth required, and the trencher breaks the hard layers beneath. A special reclamation plow may also be used. With this plow, the sod, sometimes together with the topsoil, is removed and brought over the open furrow on the subsoil, which has been turned over by the same plow.

If leveling on a rather small scale is necessary, the subsoil of the higher spots is dug from the open furrow by hand and transported to the lower spots. For large-scale leveling, bulldozers and draglines may be used. The sod and the topsoil are removed first. Then the subsoil is leveled by the bulldozer or is excavated from the high spots by draglines and transported by dumpcarts to the



FIG. 3. RECLAMATION BY HAND

spots to be raised. The sod and topsoil are replaced by bulldozers. Afterward, the soil must be plowed because of its compaction by the bulldozers.

After the plowing and leveling operations, the soil is disced to cut the sod and break large lumps of hard earth as well as to mix sod and topsoil.

Reclamation by hand power (fig. 3) provides the greatest assurance that each layer of soil is properly placed and that leveling operations are carried out with the utmost care. This, however, was not the real reason for the initiation of reclamation by manual labor, as the increased value of the land never compensates for the extra cost. The real reason was to provide jobs for laborers who were, at least temporarily, unemployed. High subsidies were paid to reclaimers for this work.

In reclamation by manual labor, there are generally three pits in operation: one from which the sod has been removed, together with a small quantity of any

topsoil that may be present; one from which the bleached sand has been removed; and one that has been excavated to the desired depth. The different layers are replaced as follows: At the bottom of the third pit is placed the bleached sand from the first pit. On this is placed a layer of red sand, about 0.1 m. thick, from the second pit. Then the red sand is covered with sod from a new pit. Finally a layer of red sand, about 0.2 m. thick, taken from the second pit, is placed on top of the sod (fig. 4).

It is best not to place all of the sod between the two layers of red sand, but rather to put one third to one half of it on the surface. This will prevent drifting of the sand and ensure more thorough mixing with the sod.

If the spade depth necessary for best rearrangement of the layers is insufficient to break up underlying impermeable layers, the subsoil on the bottom of the open furrow is also loosened.

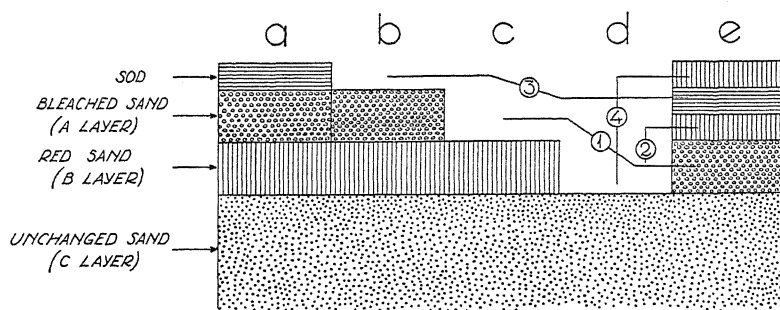


FIG. 4. DIAGRAM OF HEATHLAND RECLAMATION BY HAND

a. Natural profile. b. First pit, from which the sod has been removed. c. Second pit, from which the bleached sand has been removed. d. Third pit, excavated to the desired depth. e. Reclaimed profile. The figures denote the sequence of the operations.

If, besides spading, leveling is necessary, this must always be done by digging the subsoil out of the high spots and mixing it with the subsoil of the low spots. The soil is commonly transported in wheelbarrows or in dumpcarts pushed by hand or drawn by horses or portable engines. The wheelbarrow boards or the rails are laid on the soil that has already been treated.

RENEWED RECLAMATION

Reclamation may be renewed on plots that formerly were reclaimed by a less effective method than that now in use.

The need for renewed reclamation must be great to warrant the undertaking of such a project, because the cost involved is almost as great as that of reclaiming wasteland. Suppose, for example, that the productivity of wasteland is nil; good reclamation can make this land 100 per cent productive. A tract of land to be reclaimed anew, however, may already have a productivity of 50 per cent; the operation, therefore, can raise its productivity no more than 50 per cent. When costs are equal, then, the financial returns from renewed reclamation will be only about half the returns from an original reclamation. This means that

renewed reclamation demands greater accuracy, since faulty execution will have more serious consequences.

Reclamation commonly is renewed under the following circumstances:

1. If a hard layer is present as a result of failure to break up the iron-humus pan during the original reclamation. If the profile shows no other faults, plowing by underground trenchers will give satisfactory results.
2. If the succession of the layers in the profile is wrong, for example, when bleached sand still occurs immediately under the topsoil and red sand of good quality is found in the next layer. If there is a tough sod, a reclamation plow can be used. If not, it will be impossible to bring the topsoil over the open furrow. If there is no sod, the topsoil is removed by a bulldozer, then the subsoil is plowed to bring the red sand to the top with the bleached sand at the bottom. Finally, sod and topsoil are replaced.
3. If topsoil or subsoil or both are irregular in composition. In this case the topsoil or other layers are usually of unequal thickness. The following difficulties arise from such irregularities: (a) unequal fertilizer requirements; (b) great differences in the growth of plants and in the time of ripening; (c) marked variations in moisture content, as a result of which some places are too wet in spring whereas others are too dry in summer. Although these irregularities can be corrected mechanically, the operation requires such exactitude that hand power is preferable.
4. If the land is not level. This is likely to occur when the original reclamation consisted only of tillage, usually by plowing. In low spots crops may suffer from excess water, whereas in the high spots symptoms of desiccation are evident. The surface must then be leveled by the methods previously described.

If two or more of the aforementioned faults are combined, the advantages of mechanical improvement increase. Indeed, the financial returns from breaking up impermeable layers and leveling the surface generally are far greater than those accruing from putting the layers in proper succession and dividing the topsoil regularly.

Though the correction of combined faults by hand power is very expensive, it may increase the value of the land so much that renewed reclamation may yield greater financial returns than would correction of individual faults. Where the productive capacity of the soil is of greatest significance and the placing of unemployed laborers is considered desirable, renewed reclamation by hand is certainly justified.

CULTIVATION

As soon as the soil has sunk sufficiently, the first crop can be planted. A normal crop can be grown immediately after application of 60 tons of compost per hectare together with large quantities of commercial fertilizers and lime. This procedure, however, may be risky; furthermore, it may be many years before the topsoil is in good condition.

It is recommended, therefore, that after reclamation, a green manure crop of yellow lupines (*Lupinus luteus*) and serradella (*Ornithopus sativus*) be grown first. In preparation, 20 tons of compost or farmyard manure per hectare is applied to stimulate growth of soil microorganisms. Then 2,000 kgm. of marl, 1,000 kgm. of basic slag, 500 kgm. of muriate of potash (40 per cent K_2O), and

100 kgm. of a mixture of equal parts of ammonium nitrate and chalk are applied. As newly reclaimed soils often show copper deficiency, 50 kgm. of copper sulfate per hectare is also applied.

A mixture of 80 kgm. of yellow lupine and 20 kgm. of serradella seed is sown as early as possible. When these plants are in full growth and have not yet ceased blooming, the crop is plowed under. After the loose soil has had time to settle thoroughly, a succeeding crop, preferably rye, is sown.

Ever since commercial fertilizers were introduced, lack of water has been the limiting factor for crop production on the high sandy soils. Not only the yield but the choice of crops is affected. These drawbacks can be overcome by sprinkler irrigation during dry periods, the water being drawn from deep wells. This technique is gradually spreading.

RECLAIMED PEAT SOILS AND THEIR AGRICULTURAL IMPORTANCE

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Peat is found in many parts of the Netherlands. The peat layers in different districts vary rather widely in development and position. Consequently, their values for peat-making and for reclamation differ in the several regions. On the basis of these two potential uses, the Dutch peat soils may be classified as *low-moors* and *highmoors*. These two terms by no means define the quality of the peat; they merely indicate that under present conditions the former lie only slightly above the water level, whereas the latter are high above it.

PEAT DISTRICTS

The Netherlands may be divided into the following peat districts (fig. 1):

1. Low peat soils in the west. This is the so-called Holland-Utrecht peat district, which occupies large parts of the provinces of Utrecht, Noord-Holland, and Zuid-Holland. This district used to be considerably larger, but the regions where peat still occurs at the surface have been markedly reduced by the sea, which has eroded away large areas and has covered others with recent marine clay sediments.
2. Low peat soils in the north. These soils are found in the northwestern part of the province of Overysel and in the southern and central parts of the province of Friesland.
3. High peat soils in the north. These soils are found in the provinces of Groningen, Drenthe, and Overysel near the German frontier.
4. High peat soils in the southeast. This is the so-called Peel district, lying on the borderland between the provinces of Noord-Brabant and Limburg.
5. Scattered low peat soils in the Pleistocene sandy areas. In contrast with the aforementioned districts, each of which occupies a large area, many scattered small moors varying between 0.5 and 10 hectares are found on low places of the sandy regions in the eastern and southern part of the country.

GEOLOGICAL DEVELOPMENT

Geologically, the peat soils in the Netherlands are very young formations. The oldest date from interglacial periods and belong, therefore, to the Pleistocene epoch. They are of minor importance for reclamation.

In the boreal period (8000-5000 B.C.) an important peat formation began. The peat developed on the Pleistocene coversands, which slope gently from the hills in the province of Utrecht to the present North Sea. It developed as a ground-water peat under the influence of the slow rise in sea level, a process which continued until the middle of the Atlantic period. Then the sea invaded this peat district, partly covering it with thick layers of sand and clay. This so-called formation of *old sea clay* dates from the mid- and late-Atlantic period (3500-2000 B.C.). Because of recession of the sea in the next period—the sub-boreal—new peat could form in the district that now includes the western part

¹ Dutch Heath Reclamation Company.

of the Netherlands. In that region this peat is called *surface peat*, in contrast with the peat lying under the old sea clay and known as *peat lying at a greater depth*. Conditions in the subboreal period were such that peat could be formed on a large scale also on the coversands in the northern, northeastern, and south-

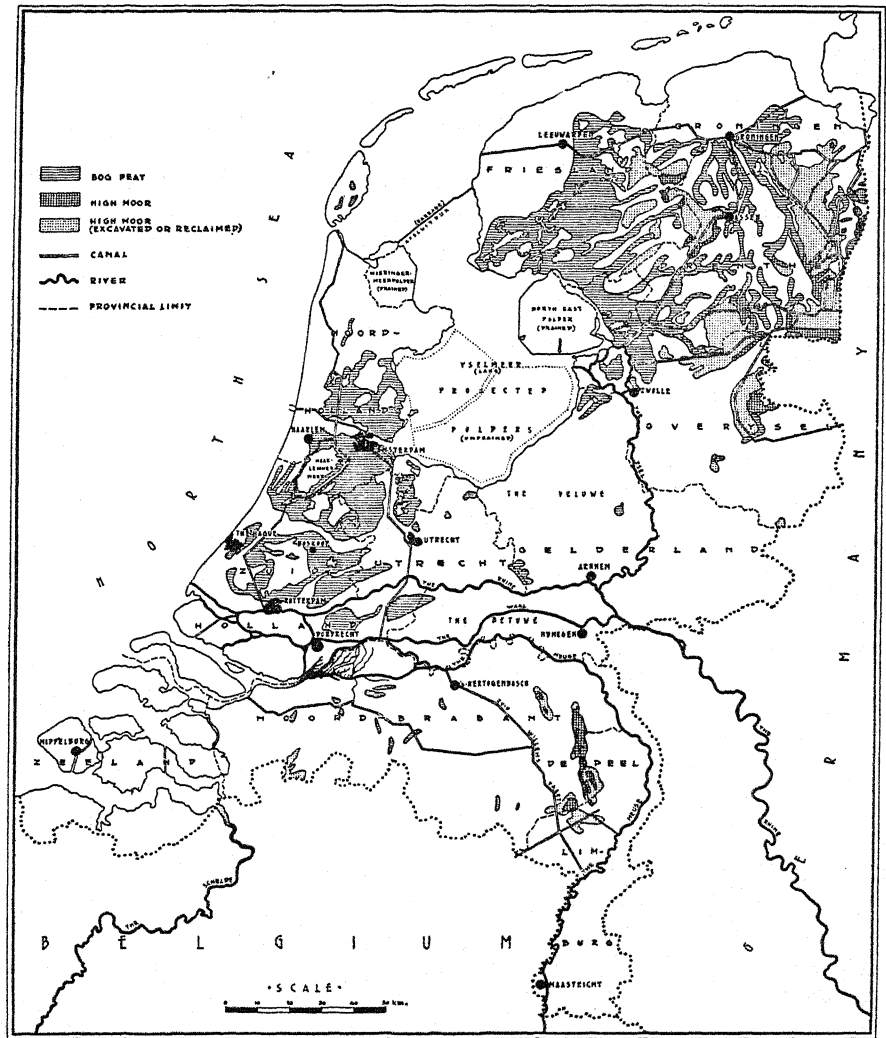


FIG. 1. MAIN PEAT DISTRICTS OF THE NETHERLANDS

eastern part of the country. These peat formations grew continuously until almost the present day. An interruption occurred, however, at approximately the transition from the subboreal to the sub-Atlantic period. During this time the so-called limitation layer of Weber was formed between the ancient moss peat of subboreal period and the recent moss peat of the sub-Atlantic period.

In the western region, this sub-Atlantic peat has not reached full development

because it was covered by a deposit of young marine clay. Figure 2 represents this development in the western part of the Netherlands.

In districts where the old sea clay is absent and the surface peat rests directly on the peat lying at a greater depth, the organic sediments are very thick. Near Amsterdam, these strata are about 13 m. thick, the layer of surface peat being 4 to 7 m. In the western part of the peat district the Atlantic clay sediments are about 10 m. thick. The peat lying at a greater depth is found here at about 14 to 16 m. below N.A.P.² This peat, which originally was very thick, has been compressed by the younger sediments to a layer of about 0.5 m.

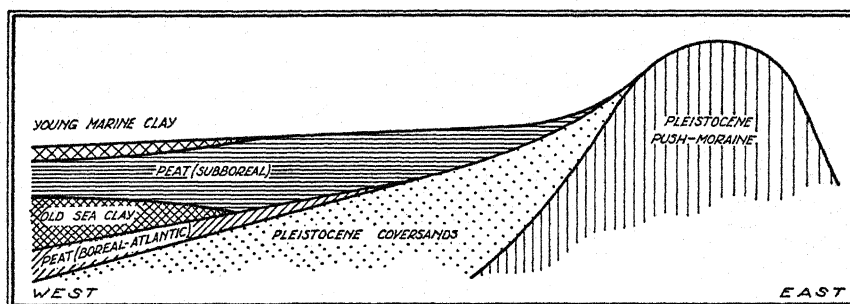


FIG. 2. CROSS-SECTION THROUGH THE WESTERN PART OF THE NETHERLANDS

BOTANICAL COMPOSITION

Obviously, the botanical composition of peat depends on the plant communities that once existed. These communities are, in turn, related to the quality of the water at their disposal. If this water is rich in nutrients, a eutrophic peat will form. It will be a reed peat; a forest peat, as found in the tidal river district; or an alder bog peat, the vegetation in the brook valleys. Water poor in plant nutrients (rain water) gives an oligotrophic peat formation, moss peat. The intermediate formation is mesotrophic, sedge peat. The various kinds of peat are named after the principal representatives of the plant communities.

Reed peat consists mainly of reed (*Phragmites communis*). This kind of peat indicates nutrient-rich water as well as a certain influence of the sea. Because of its high content of pyrites, this kind of peat is not suited for reclamation. Forest peat contains many remnants of wood from oak (*Quercus robur*), ash (*Fraxinus excelsior*), willow (*Salix alba*), and alder (*Alnus glutinosa*) and is somewhat silty.

Sedge peat consists of various species of *Carex*, and seeds of *Menyanthes trifoliata* are present. Besides remnants of alder, alder bog peat contains remnants of different *Carex* species.

Moss peat may be formed from many kinds of *Sphagnum* together with remains of heather (*Calluna vulgaris* and *Erica tetralix*) and cotton grass (*Eriophorum polystachion*).

Climatic changes and the flooding and recession of the sea frequently dis-

² N.A.P. is a standard level about as high as mean sea level.

turbed the regular building up of the peat. Side by side with the normal development from eutrophic through mesotrophic to oligotrophic sediments, all sorts of transitions may appear in other sequences according to prevailing conditions.

LOW PEAT SOILS IN THE WEST

Peat-making

The peatlands of the western part of the Netherlands were put to use as pastures at a rather late date, from the 11th to the 14th century. Scarcely had the land been converted to agricultural use, when peat-digging started. This must be attributed to the scarcity of woodland in the Netherlands, which resulted in a lack of fuel. Dried peat has a high caloric value and was generally used as fuel in the Netherlands until the beginning of the 20th century. At first, peat was dug by hand. At the end of the 19th and the beginning of the 20th century, manual labor was replaced by mechanical power. Peat for fuel should have a low silt content. The districts in which peat was dug in the western part of the Netherlands consisted of moss peat and slightly silty forest peat.

Removal of the peat left a lake. Small strips of land, however, were spared. On these, the peat was placed to dry.

Peat-making has always been more or less regulated. The regulations dealt with the proportion of land to the water accumulations that finally would develop. Sometimes these regulations were not obeyed, and the small strips of land were also dug out. Then large areas of water, such as the Haarlemmermeer, came into existence. Wave action, due to the prevailing westerly winds, especially at the eastern sides of the lakes, caused a gradual crumbling of the banks, so that villages and towns, such as Amsterdam, were endangered. Peat-making in the western part of the Netherlands has always been at the expense of existing cultivated land, much of which was of good quality.

History tells us that all towns in the western part had peat markets. One of the oldest is that of Dordrecht, which dates from the year 1377.

Figure 3 shows a district in the western part of the country in which peat is being dug out.

Drainage

In the 17th century when windmills had proved their usefulness, it became possible to drain the pools created by peat-digging. At first, only the smaller lakes could be drained; in the course of the next centuries, as a result of further technical progress, the larger ones also could be treated. At the end of the 18th century and the beginning of the 19th, steam engines were used. Diesel and electric power followed in the 20th century. The drainage methods are described elsewhere in this issue.

Generally the polder level of the lake thus reclaimed is several meters lower than that of the nonexcavated peat districts in the neighborhood.

Reclamation

The bottom of the former lake, now drained, may consist of the following kinds of soil: (a) peat to a great depth, or a thick layer of peat on a clay subsoil;

(b) a thin layer of a peat on a clay subsoil; (c) clay with some peat at the edges; (d) sand with a thin layer of peat in places.

The layer of peat that may be found on a lake bottom consists of remnants of this material which were lying at too great a depth to be dug out and which

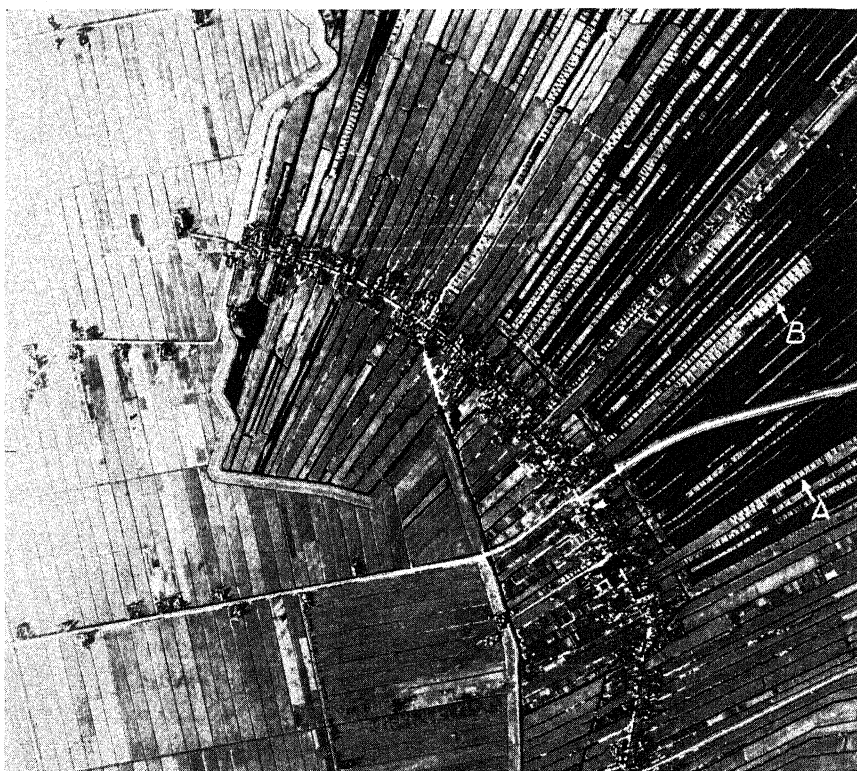


FIG. 3. AERIAL VIEW OF A REGION IN WHICH PEAT DIGGING IS IN PROGRESS

On the right, existing grassland is being dug out for peat-making and turned into a lake. On the narrow strips of land that remain, the peat is dried. At A, a black mass of dredged peat is spread out to dry; at B, blocks of peat have been piled up.

On the left, all the peat was dug out. The lake that remained was drained and its bottom reclaimed. In consequence, the land is several meters lower than that on the right.

From a file of aerial photographs of the Soil Survey Institute, Wageningen. Photo Allied Air Force, September 16, 1944. A part of this photograph was published in C. H. Edelman's "Soils of the Netherlands," North Holland Publishing Company, Amsterdam, 1950.

were not beaten away later by wave action. The clay layers belong to the old sea clay formation. The sand belongs to the Pleistocene coversands.

The method used for reclaiming the drained land depends on the quality of the material present, as the future use of the soil is closely connected with this.

Peat soils or thick layers of peat on clay subsoils. Marked differences in surface levels generally occur in deep peat on clay. Regardless of these irregularities, the peat must be well leveled to bring the surface to the right height in relation

to the water table. During the leveling, the peat must be loosened thoroughly, either by plowing or by spading. It is important to level in such a way that the water table in all parts of the polder may be 40 to 50 cm. below the surface. If the water table is lower, the peat may dry irreversibly. If this occurs, it can absorb scarcely any water, and its agricultural value will be virtually nil. This fault frequently becomes apparent in polders that originally were improperly reclaimed. Subsurface irrigation through tile drains, combined with thorough control of the height of the water in the ditches, may be the solution in these cases. The former topsoil was generally thrown into the lake, as it was not suitable for fuel. Sometimes it is found after the lake has been drained. If possible, it is used again as topsoil.

Thin layers of peat on clay subsoils. The differences in surface levels are due not only to the residual peat but also to the quality of the clay subsoil. Differences originating in the clay subsoil are caused by the system of tidal creeks separated by basins in the old sea clay formation. The sediments of silt and silty clay in the former tidal gullies sink only slightly, if at all, whereas the heavier sediments of soft clay in the basins settle considerably. This may result in differences in height of a meter or more. The soils in the former creeks, moreover, are calcareous and of good quality, whereas the soft clay soils are acid and of poor quality. In reclamation, this calcareous clay soil may play a prominent part. If there is a sufficient quantity, it can be used for soil improvement. In leveling the surface, it can be transported to spots where peat still occurs, generally on noncalcareous clay. The calcareous clay should be deposited to a depth of about 25 cm. Of course the peat must also be leveled. Thus productive arable land can be made. In such cases it must be drained to a depth of 1.25 to 1.50 m. If there is only a small quantity of calcareous clay, part of the polder can be transformed into arable land and the rest into grassland. The polder level must be varied according to the circumstances.

Polders with clay soils. After the polders have been drained and parceled, their reclamation is virtually finished. The clay soils, the properties of which are described elsewhere in this issue, can be used for cultivated crops and for grassland. Generally, peat layers of varying thickness are still found locally near the edges. These layers can be reclaimed for use as grassland in the manner already described.

Lakes with sand bottoms. As a rule, lakes with bottoms of Pleistocene sand, sometimes covered with thin layers of peat, will not be reclaimed. The sandy subsoil is so permeable that after drainage of the lake, water from the surrounding areas will seep into the new polder. This seepage is aggravated by the proximity of the high hills in the east. In consequence, the drainage cost is too high for profitable agriculture. The lakes, therefore, remain in existence, and many of them, such as Loosdrecht, are well-known water sports centers.

Agricultural importance of reclamation

The peat soils are used almost exclusively for grassland. They are not suitable for permanent pastures because the soil is so soft that after a few years it be-

comes closely packed. Moreover, irregular shrinkage occurs frequently. The soil, therefore, is plowed every 10 or 15 years and then cultivated for 1 year. Small grains are commonly sown as a nurse crop for grass.

Soils formed of calcareous clay spaded on a layer of peat or those that consist wholly of calcareous clay are used exclusively for arable land. Their yields are among the highest in the Netherlands.

The noncalcareous silty clays are also cultivated. If they are not decalcified to too great a depth, the calcareous clay from the subsoil may be brought up by deep spading or by treatment with a trenching plow. The soils may be considerably improved by these treatments.

The heavier noncalcareous clay soils are generally used for grassland, as are the thin peat layers covering soft clay. This so-called cat clay, described elsewhere in this issue, is usually very acid because of its ferrous sulfate content. In general, this kind of subsoil has an unfavorable influence on crops.

Westward, the agricultural quality of the old sea clay gradually improves. Naturally, therefore, the drained lakes in the east of this district are grassland polders, whereas the polders in the west are used as arable land. Between them there is a gradual transition with mixed farming.

The thickness of the residual peat varies in places, since some of the earliest reclamations were not carried out properly from an agricultural standpoint. Many of the polders, therefore, have been subjected to renewed reclamation, consisting of leveling and digging out of local peat areas. The object of these operations is to improve irreversibly dried soils and other poor patches of land.

Significance of special cases

Because pieces of peat on the eastern shores of rather extensive lakes are often eroded away, as are remnants of peat still present in the lakes, great quantities of peat may disappear. In the Haarlemmermeer alone, 200×10^6 cu.m. of soil was eroded away. Not all the peat is destroyed or oxidized; a part of it is carried over the bottom by countercurrents and finally accumulates on the western side as slush or muck.

Slush, a calcareous silty peat, is formed by blending of the original peat with the silt of the argillaceous lake bottom and by enrichment with lime from mollusks. When the lake is drained, the slush forms valuable soil for horticultural purposes. Yields on such soil are high and of prime quality.

Muck also is of great value to horticulture. Neither vegetable growing nor arboriculture is possible on peatlands without regular use of muck, which is dredged out of existing lakes or is dug from ground that has already been reclaimed.

Although muck and slush are used only on small areas, they are of great importance to the culture of horticultural produce for export.

LOW PEAT SOILS IN THE EAST

Peat-making

Peat-making operations in the east are similar to those in the west.

Drainage

The only difference between drainage in the east and that in the west is that, in general, the lakes in the eastern section were not drained until the present century, and therefore only modern methods have been used. The windmills that are so characteristic of many reclaimed lakes in the western part of the Netherlands are not found in the east.

Reclamation

Old sea clay is absent in the low peat areas of the east, and the soils are composed of peat remnants on a subsoil of Pleistocene coversand. The differences in surface levels in these regions are due to the irregularity of the peat remnants. Variations in the level of the sandy subsoil are of minor importance.

The peat must be leveled and loosened. Similar operations must also be applied to undecomposed or partly decomposed remnants of plants that grew in the lake before reclamation. Afterward, these remnants may cause a considerable sinking of the surface.

As the peat cover is generally thin, sand usually comes up when the ditches are dug. This sand is used to cover the peat and thus make the topsoil more solid. For reasons already mentioned, considerable quantities of seepage water are to be expected. To reduce seepage, the ground-water level is kept as high as possible, usually at a depth of 40 to 50 cm.

Agricultural importance of reclamation

The areas reclaimed in this way are used exclusively for grassland. Yields are high because of a favorable profile for development of sod.

HIGH PEAT SOILS IN THE NORTHEAST

Peat-making

When peat was dug for fuel in the west, good quality grassland was destroyed. This has not been the case in the northeastern peat districts. Here the moors were wasteland, and those that are left are still in this condition.

In the beginning, in the large peat district along the German frontier and in the smaller one along the Frisian-Drenthian frontier peat was dug only to supply local fuel needs.

About the year 1600, this so-called *wild* digging gave place to systematic peat-making by the town of Groningen to supply fuel for its inhabitants. This operation required the digging of an extensive system of canals to drain the moors and to provide means for transporting the peat. These canals cut into some of the sandy subsoil of the peat deposits. Excavation of the peat was strictly regulated to maintain its quality. Recently formed moss peat (the so-called *bolster*) has a much lower caloric value than the ancient moss peat or the sedge and reed peat (the so-called *black peat*) in the subsoil. The regulations therefore prescribed that a layer of bolster, 50–60 cm. thick, be thrown back. The rest of the peat was dug out down to the subsoil of coversand. Later it became evident that the throwing back of the bolster had been of special value to agriculture. Peat-

making is still in progress, but the area of land now available for excavation is small.

Reclamation

When the peat-making operations in a moor ended, the land consisted of a topsoil of bolster, 50 to 60 cm. thick, on a subsoil of coversands. Moreover, the excavated sand had been deposited along the canals. On this land the bolster was spaded and leveled as much as possible, and on it was spread a layer of sand, 12 to 15 cm. deep, taken from the canals (figs. 4 and 5).



FIG 4. THE BOLSTER, LEFT BEHIND AFTER PEAT-MAKING, IS COVERED BY A THIN LAYER OF SAND

Thus a profile very well suited to agricultural use came into being. The sandy topsoil ensures easy tillage of the ground, and the peat subsoil forms an inexhaustible reservoir of moisture. The significance of the bolster is becoming increasingly evident, for this young moss peat does not dry irreversibly and can always be remoistened. Careful control of the ground-water level is essential. A water table at a depth of 50 cm. has proved to be most effective. Some technical construction is necessary for water regulation, as the district slopes in a westerly direction.

Nowadays, reclamation follows certain basic principles. In the past, this was not always the case. Then the necessary care in the throwing back of the bolster was not always taken, and sand of poor quality was sometimes used. As a result, bad spots are found.

After reclamation, the sandy topsoil is low in humus. The plowing up of a thin layer of bolster at regular intervals develops a humic topsoil, which is a thorough mixture of sand and of bolster that gradually changes into mold.

The parceling of these districts depends entirely on the canal systems constructed for peat-making. These canals determine the position and the width of the farms. The distance between the canals is generally 150 or 160 m., and the farms usually consist of 25 to 30 hectares. They are, therefore, very long and narrow.

Agricultural importance of reclamation

Fertilization. When reclamation is completed, the sandy topsoil is still lacking in plant nutrients. Fertilization is necessary. In the old days, manure in the form of town compost was applied. Ships transporting peat to the town of Groningen

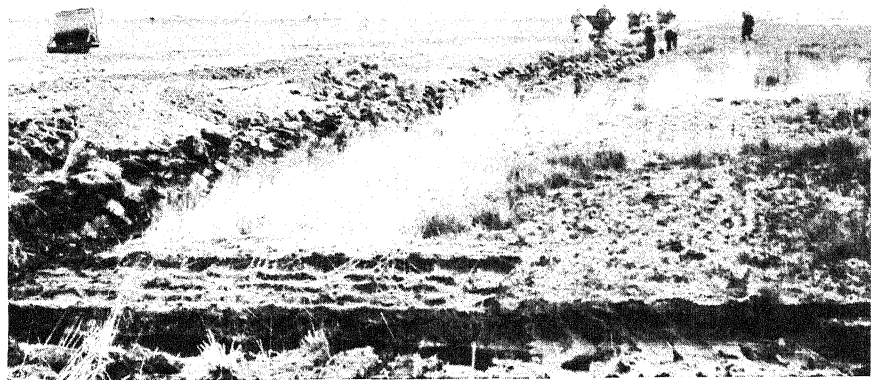


FIG. 5. THIS BOLSTER HAD BECOME OVERGROWN WITH HEATHER BEFORE THE LAND WAS RECLAIMED

also carried compost as a return cargo. This material could easily be transported by canal to the parcel where it was needed.

At present, the application of compost has given way to the growing of green manures and the use of commercial fertilizers and lime. A basic application of 1,000 kgm. of potash (40 per cent K_2O) and 800 kgm. of basic slag per hectare and about 50 tons of compost is common on newly reclaimed land. Large quantities of fertilizers are also applied yearly. Nowhere else in the Netherlands is the consumption of fertilizers per hectare of arable land so high as on these reclaimed peat soils.

Crops. Potatoes for industrial use are considered by far the most important crop. The main product is starch, from which numerous other products are made. Potato yields are frequently as high as 35,000 kgm. per hectare.

Rye and oats are the next most important crops. They are grown not only for

grain but also for straw, which is used in the manufacture of cardboard. Mangolds are of interest in crop rotations, and some oil seeds also are produced. The soils are well suited to truck farming and produce good yields of prime quality.

Grassland is of minor importance, for the reclaimed peat soils are primarily in districts where cultivated crops are paramount.

In view of the great number of favorable qualities of these soils, which are sometimes called *dal* soils, it is no wonder that this region, which used to be a worthless moor, has become a thriving farm district.

HIGH PEAT SOILS IN THE SOUTHEAST

Peat-making

In the southeast district, known as *de Peel*, a complex system of moors used to be found. For many centuries the farmers dug peat here for their own use. Systematic peat-making was not started before about 1860. Because of absence of regulations, all the peat was dug out, and today the ancient subsoil is lying on top. Only in spots have remnants of peat been left. Moreover, this is not bolster but, rather, black peat.

Reclamation

The land to be reclaimed here is very irregular in composition. The surface of the sandy soils is far from level. The peat remnants, too, are full of pits and holes, and the black peat is subject to irreversible drying. In digging and leveling the land, the danger of irreversible desiccation of the peat is very great. It is necessary, therefore, to cover the peat with a layer of sand about 20 cm. thick to avoid plowing up of the peaty subsoil. Because of the height of this land, the water table falls to a great depth, and this, together with the presence of black peat, makes the soils too dry in summer.

The sand used to cover the peat does not come from canals but is removed from the sand ridges that are common in this district. In many places it must be transported for a distance of 1 km.

As peat and sand alternate within small areas in *de Peel*, reclaimed land nearly always consists of a combination of peat soils and sandy soils.

Agricultural importance of reclamation

Fertilization. Because of the absence of a good system of canals, there has never been any intensive traffic in *de Peel*. Consequently, composts were not applied so extensively in former years as in the northern district. In *de Peel*, the manure on farms already in existence was generally reserved for the newly reclaimed land. Today green-manuring is a general practice.

The yearly fertilization is about the same as that on the sandy soils in the neighborhood.

Crops. Among the rotation crops, rye and oats occupy a prominent place, followed by potatoes. The yields are smaller than in the north, because the water-holding capacity of the soils is lower. On the somewhat lower land of better quality, mangolds are grown rather successfully. The lowest spots are devoted to grassland.

FAULTS IN RECLAIMED HIGHMOORS

Peat dust

Remnants of dried peat are commonly left on the highmoors. If these irreversibly dried peat lumps occur in great quantities they may adversely affect the water-holding capacity of the reclaimed soils. As many as possible of these remnants should be gathered and removed.

Reclamation disease

As the topsoil of reclaimed land is lacking in the major plant nutrients, quite possibly it is also low in minor elements. Obviously, the poor growth on the reclaimed soils in the first few years must be attributed to a lack of copper. This can be remedied by fertilizing the soil with 50 kgm. of copper sulfate per hectare or with 250 kgm. of finely ground copper slag.

SCATTERED BOG PEATS

Peat-making

On most scattered bogs the peat has been dug out by farmers for their own use. In only a few places has the removal been systematic. As a rule, existent grassland has been dug out.

Reclamation

Reclamation of these small bogs is of minor importance, and little has been done along these lines. Many farmers fill their peat holes with sand, but a few have reclaimed their land by loosening and leveling the peat and covering it with sand.

Agricultural importance

Once the peat has been removed, these scattered bogs are resown to grass, usually with oats as a nurse crop.

RECLAMATION OF DUNE-SAND SOILS

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In the beginning, the dune-sand soils in the Netherlands were almost entirely overgrown with forest. This was a xerophytic *Quercus-Betula* association which had a high calcium requirement. The original calcareous sands, therefore, are decalcified to a great depth. Subsidence of the land and rising of the sea level have been serious problems in the dune-sand areas.

Archaeological discoveries and historical information have shown that the early population reclaimed the soil in the lower places for growth of cultivated crops and for grassland. The highest parts became uncultivated wastelands.

The dune-sand soils in the Netherlands are in the neighborhood of large towns. Growth of these towns after the late Middle Ages required a great deal of sand, which was excavated from the dunes. In time, it became evident that the excavated areas were well suited to vegetable and flower-bulb growing. These areas, therefore, have been in great demand during the last few centuries. In fact, the demand for them grew faster than the rate of excavation. In the 19th century the dune-sand soils were found to be suitable for the making of lime-sand bricks. At the end of the century a brick factory was established, and the sand, especially in the ancient dunes, was rapidly removed.

Today the dunes have been almost completely excavated and put under cultivation. Only a few scattered areas are still in their natural state (fig. 1).

MORPHOLOGY

In the Netherlands there are two types of dunes: ancient and recent. The ancient dunes are decalcified to a great depth; the recent ones, to a slight depth and only in some places. The ancient dunes date back to the Atlanticum (a moist period from 5000 to 2000 B.C.) and have retained perfectly the shape of a sand reef. Though they look somewhat wind-blown, the base of the formation is still the sand reef. The recent dunes are of historical age. Essentially, they also were formed as a sand reef but later were blown inland over the landscape. Thus they are composed entirely of aeolian sand. Locally, they have been blown to a height of about 60 m. These recent dunes now form a sea barrier along much of the Dutch coast. The ancient dunes usually lie behind the younger ones, in places at a distance of several kilometers and in other places very close. Some of the ancient dunes run parallel with the recent dunes; some bend outward and are covered by the recent dunes. The ancient dunes have a maximum height of only 4 m.

SOIL CONDITIONS

The Dutch dune-sand soils consist of moderately coarse grained calcareous or noncalcareous sand. Soils of prime quality are found on the ancient excavated

¹ Dutch Heath Reclamation Company.

dunes with the best developed profiles. They have a homogeneous layer of calcareous sand 4 or 5 m. deep. These are the ideal soils for bulb growing. For

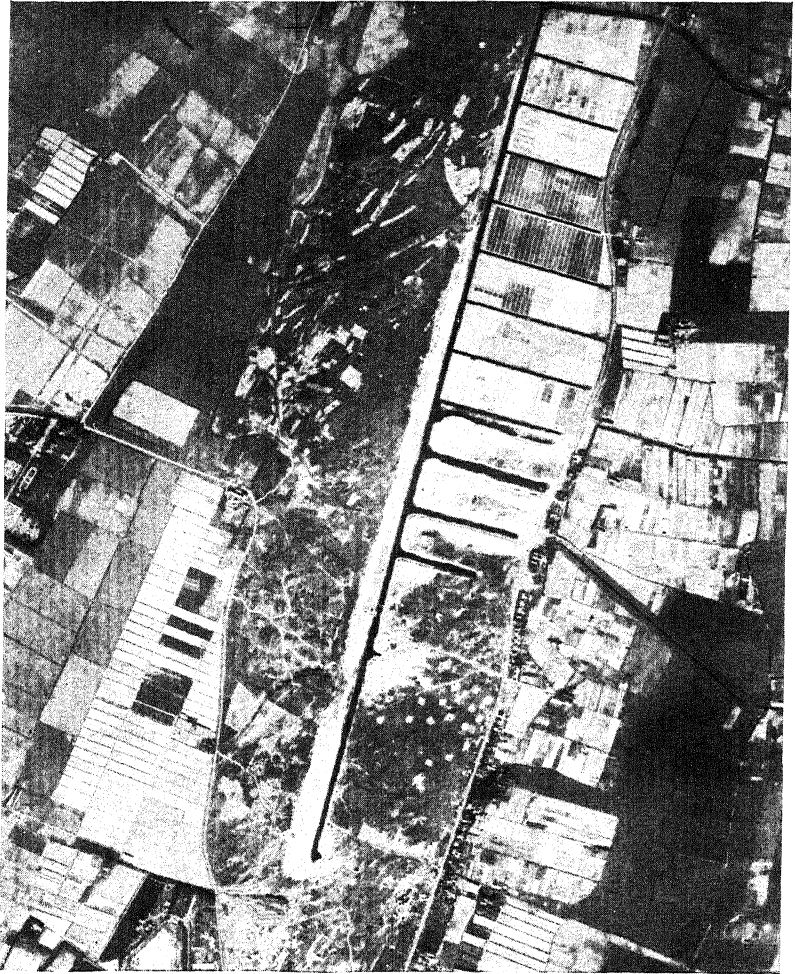


FIG. 1. AREAL VIEW OF PART OF THE ANCIENT DUNES

A ridge of dunes is visible in the center running from south-southwest to north-northeast. In the southwest and along the east side of the ridge are bulb fields, which have been under cultivation for a long time.

The northeast part of the ridge has already been excavated. In the center, excavation of the original dunes is in progress.

From a file of aerial photographs of the Soil Survey Institute, Wageningen. Photo Allied Air Force, September 18, 1944.

vegetable growing, noncalcareous sand is preferred. Though some bulbs can be grown on noncalcareous sand, the financial returns are lower, for the most profitable crop, the hyacinth, cannot be grown on such soils.

The following mechanical analysis is typical of the calcareous soils: 0-16 μ , 0.5 per cent; 16-50 μ , 0.2 per cent; 50-75 μ , 0.2 per cent; 75-105 μ , 0.4 per cent; 105-150 μ , 8.2 per cent; 150-210 μ , 39.8 per cent; 210-300 μ , 41.8 per cent; 300-420 μ , 8.3 per cent; >420 μ , 0.6 per cent. The following chemical analysis is also typical: pH, 7.7; CaCO_3 , 4.3 per cent; humus, 0.6 per cent; water-soluble P_2O_5 , 20 ppm.; P_2O_5 soluble in 1 per cent citric acid, 280 ppm.; K_2O soluble in 0.1 N HCl, 80 ppm.

The noncalcareous soils have virtually the same mechanical composition as the calcareous soils, but they normally contain twice as much humus, P, and K. Because of absence of free CaCO_3 , the pH, as a rule, is below 7, and liming is necessary.

Soils with the composition of the Dutch dune sands are very permeable. The factor of permeability— K from Darcy's equation—is about 25m./24 hours. This and the insignificant adsorption capacity lead to heavy leaching of fertilizers. Application of 100,000 kgm. of farmyard manure per hectare every third year and a yearly application of 700 kgm. of superphosphate, 700 kgm. of sulfate of potash, 350 kgm. of sulfate of ammonia are normally required.

The great value of these soils for horticultural purposes depends largely on the careful regulation of boezem and polder levels, as described elsewhere in this issue. This water control, in turn, is closely related to the excavations of sand during the last century.

From the 17th century, water control in this area has been satisfactory, but in the latter part of the 19th century certain improvements were made which ensured a constant ground-water level throughout the year. This water level, 56 cm. below N.A.P. (mean sea level), is the basis for successful bulb culture. From the viewpoint of soil science, the deep homogeneous sandy profile is necessary to avoid discrepancies between the ground-water level and the water level in the drains. Profile disturbances less than 2 m. below the surface still cause irregularities in the movement of the subterranean water.

EXCAVATIONS AND IMPROVEMENTS

In the sand pits of the ancient dunes, the ultimate depth of excavation depends on the water level of the boezem or the polder in which the sand pits lie. Practical experience has shown that a surface level at 55 cm. above the water table gives the most favorable results. This was confirmed scientifically by the late Prof. A. H. Blaauw of Wageningen. Because the water table is 56 cm. below N.A.P., most of the soils are excavated to N.A.P. or 5 cm. below.

When the ancient dunes are excavated to that level they may produce calcareous as well as noncalcareous sand (fig. 2). They have had the highest altitude where they were widest, and there calcareous sand is found at N.A.P. (fig. 3). The spurs are low and narrow, and there at N.A.P. noncalcareous sand is found (fig. 4).

It is quite possible that in the highest parts of the ancient dunes, holes (wind pits) caused by secondary sand drifts will appear. As a result of these holes, decalcification may be deeper, and in these places noncalcareous sand may appear

amid calcareous sand. At first, this phenomenon was disregarded, and thus, soils poor in lime and of inferior quality would arise in the midst of good calcareous sand.

When, later, the significance of high lime content for bulb growing was realized more clearly, this problem was taken into account. Then, during the excavation of the sand, a bottle of hydrochloric acid was held in readiness so the lime content could be tested immediately. The noncalcareous sand was excavated, even if it occurred at a greater depth than N.A.P., and the hole was filled with calcareous sand taken from places where it was found above this level.

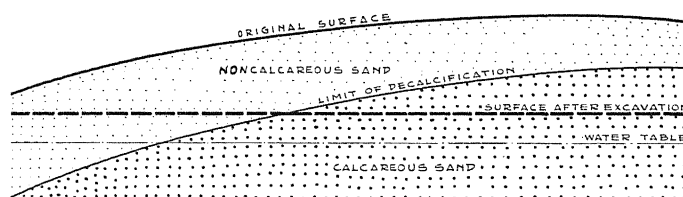


FIG. 2. LONGITUDINAL SECTION THROUGH AN ANCIENT DUNE

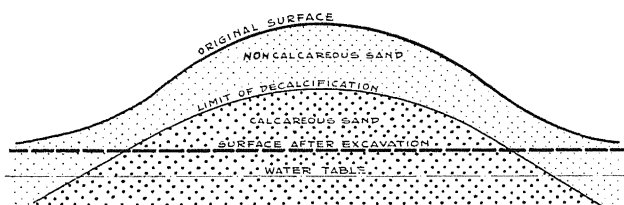


FIG. 3. CROSS-SECTION THROUGH A HIGH PART OF AN ANCIENT DUNE

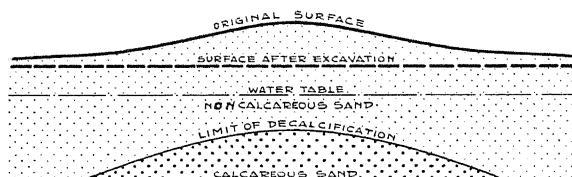


FIG. 4. CROSS-SECTION THROUGH A LOW PART OF AN ANCIENT DUNE

The low spurs of the sand reefs always consist of noncalcareous sand at N.A.P. and in some areas even to a depth of 1.5 to 2 m. below N.A.P. After excavation, therefore, noncalcareous soils always turn up on them. Since the most profitable crop, the hyacinth, requires a calcareous soil, methods were developed for raising the calcareous subsoil and removing the noncalcareous topsoil.

At present, two methods of turning soil are in use; namely, trenching and reworking with dredges. In the first method, the soil is excavated by hand (fig. 5), the trench being kept dry by pumping the subsoil water from deep wells. In the second method, the soil is turned by a dredge. The object of both methods is to turn the noncalcareous topsoil under the calcareous subsoil.

The possibilities for trenching are limited, as it is feasible to work to a depth

of only 2.75 m. below the surface because of the high water level and the marked permeability of this soil. More powerful water pumps can be made for attaining a greater depth, but the cost would be high. Where the noncalcareous profiles are very deep, it is impossible to get a sufficiently thick layer (at least 1 m.) of calcareous material on top.



FIG. 5. IMPROVEMENT OF DUNE-SAND SOILS BY HAND-TRENCHING

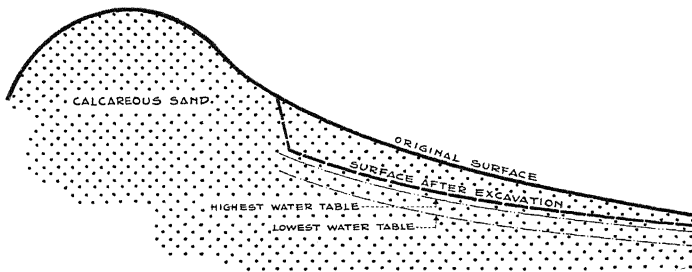


FIG. 6. CROSS-SECTION THROUGH A RECENT DUNE WITH POSSIBILITIES FOR EXCAVATION

In reworking with dredges, there is no such limitation. These machines make a trench about 10 m. deep. The method is somewhat rougher than trenching by hand, but the costs are only about half as great. Dredging will cost the bulb grower about 6,000 guilders per hectare, whereas trenching costs are estimated at about 12,000 guilders, despite the government subsidy. As both methods give good results if they are followed carefully, bulb growers generally prefer to use dredges.

These methods of soil improvement are applied not only to undisturbed sand profiles but also to the broad plains between the ancient dunes. These plains have

a sandy topsoil overlying layers of clay and peat, which, in turn, overlie the sand of ancient beaches. Besides trenching and dredging, the process of digging out the peat is used on these plains. The layers of peat and clay are removed and the hole is filled with calcareous sand, generally taken from the recent dunes. This treatment also gives good results but, like trenching, is very expensive. It requires much labor, and pumping the subsoil water is also very costly. The total costs are about the same as those for trenching.

The recent dunes, likewise, are subjected to excavation of sand and improvement of the leveled areas. The trench depth depends on the fluctuations of the water table, as in these dunes, in contrast with the older dunes, there is no constant water level. The magnitude of these fluctuations therefore determines the quality of the soil after excavation. On the one hand, the soil may not be flooded in winter; on the other hand, the water may not sink so far in summer that symptoms of drought appear.

Investigations have shown that damage from lack of water will occur if the reduction-oxidation point is deeper than 1.10 m. below the surface. This suggests that soils with an oscillation of subsoil water of more than 90 cm. should not be excavated; if they have already been excavated, they will be too dry in summer.

In comparison with the excavations of the ancient dunes, those of the recent dunes are of little importance. The recent dunes protect the low country not only from sea water, but also from salt. Their excavation would mean that the land behind the dunes would be in greater danger of salinization. The recent dunes, therefore, are excavated only in small areas where they are widest.

Sand from the dunes is used also to improve low heavy clay soils. This type of soil improvement has been carried out on a large scale in the market-gardening district of the Westland. The sand is spread over the clay soil, and during tillage some clay is worked into the sand. Eventually, the topsoil becomes a humic sandy soil with a low clay content and a thickness of 60 to 100 cm. on a subsoil of clay. This soil is excellent for the growing of vegetables. By such use of dune sand it is possible to convert two poor soils into two good ones: excavation of a dry dune-sand soil will produce a moist soil, and the excavated sand will raise the surface level of a low-lying heavy clay soil (fig. 6).

The reclamation and cultivation of the dune-sand soils have been of great value to Dutch horticulture. Both bulb growing and vegetable cultivation in the field and under glass require a great deal of capital per unit of area. For example, a hectare of deliverable hyacinths has a value of nearly 100,000 guilders. The dune-sand soils reclaimed and cultivated for the growing of bulbs cover an area of 5,000 hectares. In 1950 the bulb export from these soils amounted to more than 100,000,000 guilders. Profits from the growing of vegetables are only slightly lower per unit of area.

DRAINAGE AND RECLAMATION OF LAKES AND OF THE ZUIDERZEE

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In former times many lakes occurred in low, peaty areas in the western part of the Netherlands. Drainage of these lakes, which were only a few meters deep, became possible with the invention of windmills in the 15th century.

The first lake was drained in the 16th century, and in the 17th century lakes of more than 5,000 hectares were drained. During the 19th century, steam engines provided a new stimulus to drainage operations. Through their use, the Haarlemmermeer, a lake of 18,000 hectares, was drained. This marked the virtual completion of lake reclamation. Lakes still in existence are maintained primarily for recreational use.

A further application of the principle of lake drainage is the reclamation of land lying under water along the coast. In that case, an artificial lake is created by building a dam to enclose an area between it and the coast. This area is subsequently pumped dry. Naturally, this method is possible only along coasts that are but slightly exposed, such as those of the Zuiderzee, an inland sea in the north of the Netherlands. Earlier, some smaller polders were created in this way, and at present a large project is underway to reclaim five polders covering 220,000 hectares. Two of these polders, covering 75,000 hectares, have already been reclaimed.

According to Van Veen (10), the drainage of lakes resulted in land gains of 4,000 hectares in the 16th century, 32,000 in the 17th century, 14,000 in the 18th century, 72,000 in the 19th century, and 82,000 in the 20th century. This last figure includes the 75,000 hectares gained from the Zuiderzee. The areas reclaimed in this way are shown in figure 1.

PRINCIPLE OF FORMATION AND DRAINAGE OF POLDERS

Dutch lakes and the Zuiderzee not only help drain the surrounding country but they also serve navigation. These interests must be considered in any scheme of reclamation. An encircling canal is generally left, therefore, around the new polder. This canal remains a part of the boezem system to which the lake belonged before it was drained. Thus drainage of the surroundings and navigation are maintained. The pumping station of the new polder also can pump its water into the circular canal.

As the bottoms of Dutch lakes and of the Zuiderzee are usually 3 or 4 m. below sea level, a strong pumping station is needed. This pumping station is required not only for initial drainage but also for subsequent removal of excess water. Part of the rain fails to evaporate, and as this water cannot flow from the polder into the sea, it must be pumped out. Generally about 300 mm. has to be removed yearly.

¹ Research Department Noordoostpolder Authority.

As the bottom of the lake is usually flat or is gently sloping from the shore toward the center, leveling is unnecessary. On the other hand, there is only a limited natural flow to the pumping station, and an extensive system of water-

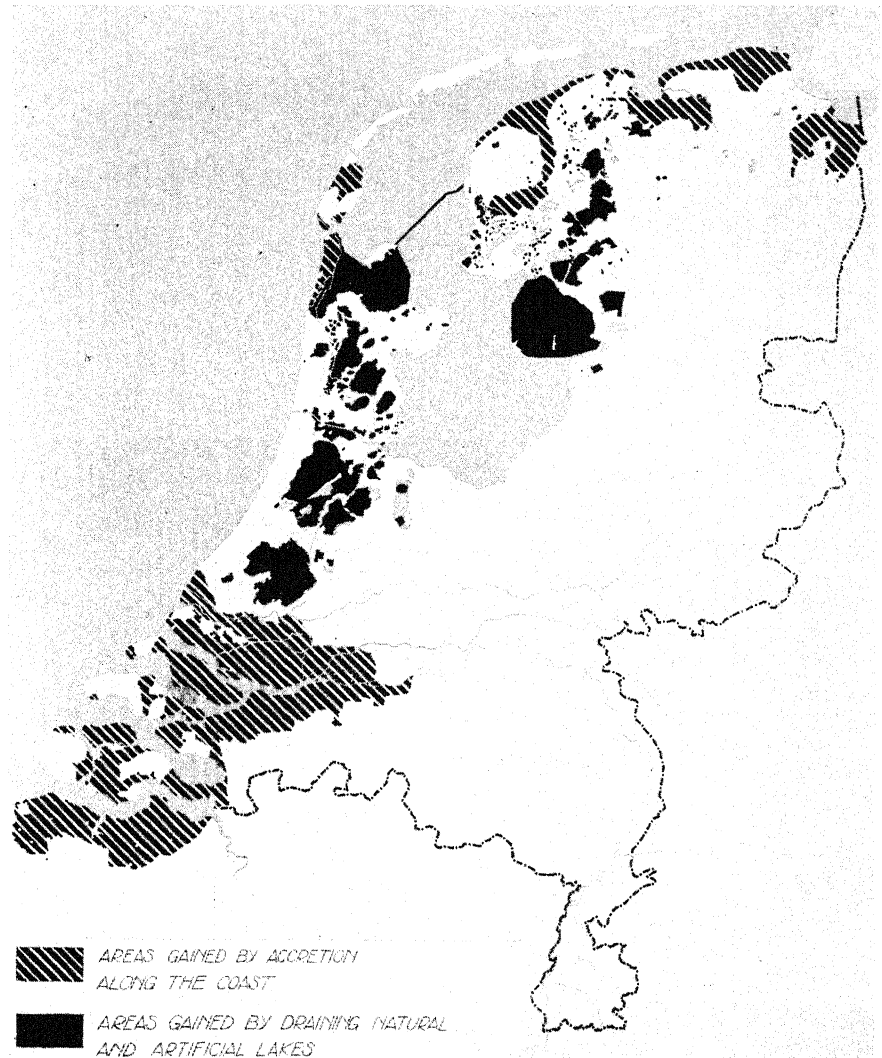


FIG. 1. LAND GAINED IN THE NETHERLANDS BY DRAINING LAKES AND PARTS OF THE ZUIDERZEE AND BY COASTAL EMBANKMENTS

ways is necessary to carry off the excess water. In large polders the higher parts have their own system of canals at a higher level to reduce the cost of pumping.

As a rule, a polder has one or more main canals, in which the pumping station maintains a constant water level. In polders used for arable farming this level is usually $1\frac{1}{2}$ m. below the surface of the lowest parts of the polder. Laterals flow

into the main canals. In the Zuiderzee polders they are spaced 1,600 to 2,000 m. apart (fig. 2). Roads are laid out between the laterals. Main ditches,² 300 m. apart, are dug at right angles to the lateral canals. Field ditches³ or tile drains, 8 to 24 m. apart, empty into the main ditches and ensure drainage of the individual fields (fig. 3).

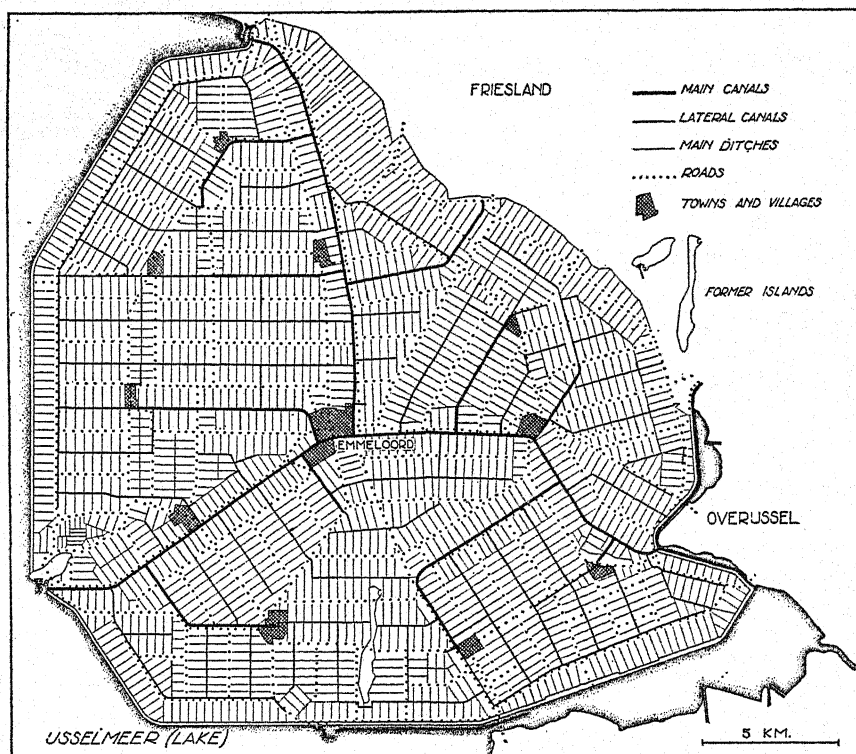


FIG. 2. MAP OF THE SECOND ZUIDERZEE POLDER (NOORDOOSTPOLDER)

GENERAL CHARACTERISTICS OF POLDER SOIL

The bottom of the Dutch lake polders is generally composed of young silt or of old sea clay.

The young silt settled on the spot and remained under water until the draining was finished. It is found mainly in the Zuiderzee area. The texture may range from fine sand to clay, according to the sedimentation conditions. Where water movement was strong, as in the narrow northern part of the Zuiderzee, the bottom is sandy. In the quiet basin of the Zuiderzee, clay was deposited.

The old sea clay is a formation of tidal flats, deposited thousands of years ago

² In the Zuiderzee polders these main ditches are about 4 m. wide and 1½ m. deep. The water level in the laterals is kept so low that the main ditches run dry in summer.

³ In the Zuiderzee polders the field ditches are 1.15 m. wide and 60 cm. deep. They are replaced by tile drains several years after the initial reclamation.

along what was then the coast but which is now farther inland because of a subsequent rise of several meters in the level of the sea. The texture of this old sea clay is heterogeneous, varying from loamy sand to heavy clay. The soil of the reclaimed lakes consists mainly of this old sea clay, as does that of one of the Zuiderzee polders.

In some of the drained lakes the old sea clay is still covered by remnants of peat. This peat developed on top of the clay. Subsequently, most of it was removed by digging and by wave action. Reclamation of these peaty areas is described elsewhere in this issue.

Like all recent marine deposits in the Netherlands, the young silt is rich in CaCO_3 . If it is clayey it contains about 10 per cent CaCO_3 . Part of the old sea

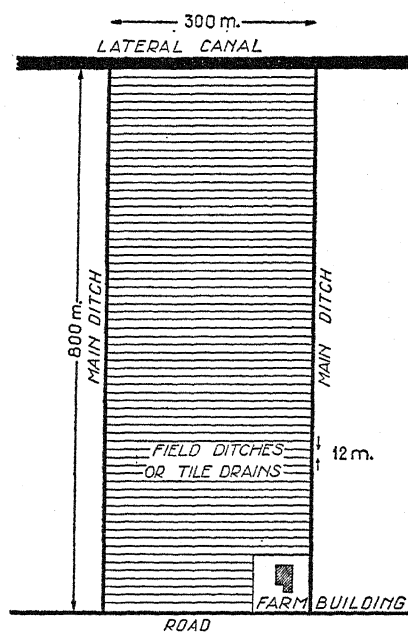


FIG. 3. STANDARD PARCEL IN THE NOORDOOSTPOLDER

clay is rich in CaCO_3 ; in fact, clayey sediments usually contain about 15 per cent CaCO_3 . The old sea clay, however, also includes a soil type poor in CaCO_3 (*katteklei*, or cat clay).

In estimating the agricultural potentialities of the newly drained areas, a knowledge of the clay content is very important. Almost all properties of the soil are closely correlated with the clay content. Table 1 shows the average contents of some important constituents of the soil. As the composition of the young silt and that of the old sea clay are very similar, in general, average values are given except for moisture and sulfur contents.

The heavier soils contain no sandy material coarser than 100μ . The content of particles smaller than 2μ forms two-thirds of the percentage of particles smaller than 16μ . This proportion is a constant property of Dutch marine soils (2).

DRYING OF DRAINED SOILS

In a sandy soil saturated with water, the moisture content is about 25 gm. per 100 gm. of dry matter. In water-saturated normal clay soils the moisture content is higher, though it seldom exceeds 35 gm. per 100 gm. If these figures are compared with those in table 1, it appears that the young polder soils retain a much larger quantity of water. The difference increases with increasing clay

TABLE 1
Composition of Zuiderzee-bottom soils just after being drained
In grams per 100 gm. dry soil

TEXTURE- CLASS	CLAY*	HUMUS†	MOISTURE CONTENT‡		SULFUR§		AVAILABLE K ₂ O¶	AVAILABLE P ₂ O ₅
			Young silt	Old sea clay	Young silt	Old sea clay		
1	3	0.5	29	27			0.010	0.007
2	6	0.9	38	34	0.1	0.4	0.017	0.010
3	10	1.5	50	44	0.3	0.6	0.025	0.014
4	20	2.7	80	68	0.4	0.1	0.047	0.025
5	30	3.9	110	92	0.5	1.3	0.068	0.035

* Particles <2 μ (determined by the method of the International Society of Soil Science).

† Determined by dry combustion.

‡ Determined by drying at 105°C.

§ Sulfur compounds soluble in a mixture of HClO₄ and HNO₃ and calculated as S.

¶ Determined as K₂O soluble in 0.1 N HCl after the carbonates have been dissolved.

|| Determined as P₂O₅ soluble in 1 per cent citric acid after the carbonates have been dissolved.

TABLE 2
Moisture content, in spring, of a soil reclaimed from fresh water
In grams per 100 gm. dry soil

LAYER	MOISTURE CONTENT				
	First year	1 year after drainage	3 years after drainage	5 years after drainage	9 years after drainage
cm.					
0-20	95	61	49	30	28
20-50	95	72	60	55	40
50-80	95	95	85	80	75

content. At a clay content of 30 per cent, for instance, the difference amounts to about 75 gm.

The high moisture content of the clayey Zuiderzee-bottom soils is due primarily to the flocculent character; the high pore volume of this structure is entirely filled with water. As a rule, the structure of this flocky mass is stable enough to prevent a loss of water by drainage. Evaporation, however, may lower the water content, and as a result, the soil will shrink, crack, and crumble.

Drying starts in the topsoil and proceeds gradually deeper into the profile. The process takes a long time, but even in the final stage the moisture content

of the subsoil will still be higher than that of the upper layers. In the latter, the drying proceeds so far that crumbs are formed. At greater depths, coarser crumbs, prisms, and columns are found successively. At a still greater depth, large cracks occur. During the first centuries after draining, no drying of any importance occurs below $1\frac{1}{2}$ m. (4). As indicated by the data in table 1, the process will be more intensive as the clay content increases. Where the clay content is lower than 8 per cent, shrinkage and crack formation are of no importance.

The process of drying depends upon several factors. Just after the draining of a new polder, when the land is still bare, the loss of water is due entirely to evaporation. Later, the drying, especially in the subsoil, depends mainly on transpiration, a process that is greatly stimulated by dry summers. Table 2 indicates the rapidity of the drying process in the young silt.

Effect on permeability

The process of drying is very important for the improvement of the permeability of the heavier soils. The permeability of the sandy soils is determined by the size of the pores between the grains. For the sands occurring in the Zuiderzee polders, the permeability— K from Darcy's equation—ranges from about 0.3 to 5 m./24 hours. The permeability of sandy soils undergoes very little change.

Just after drainage, the heavier soils form a compact mass, the pores of which are so small that the soil is almost impermeable. The process of drying, however, causes the formation of cracks, which will increase the permeability and also the water-storing capacity. As many cracks appear in the heavy soils after a number of years, the permeability is raised to as much as 100 m./24 hours. Where clay contents are lower, permeability is less. Permeability is least in soils with a clay content of 4 to 8 per cent, which is sufficient to block the pores between the sand particles but too small to cause extensive cracking.

Relation to subsidence

The drying process also causes subsidence, which may amount to as much as 1 m. in the heaviest young silts. Soils of lower clay content show less subsidence, and the phenomenon is of no importance in soils with a clay content of 10 per cent or less.

Besides shrinkage caused by drying, there is another cause of subsidence. The upward pressure in the layers that lie above the water table ceases after drainage. As a result, these layers exert a heavier pressure on the subsoil. In clay soils the resultant increase in compactness of the subsoil usually does not exceed 5 per cent; peat soils, however, may be compressed 10 or 20 per cent.

Before draining, it is desirable to have an idea of the amount of shrinkage to be expected, as the height of the future polder level is closely related to this process. This future level determines the size of several kinds of hydraulic works, such as the level of lock bottoms and the height of canal linings.

Usually subsidence is an undesirable phenomenon in polders, as it increases the depth of the polder and the costs of pumping. In areas of unequal subsidence, the flow of water to the pumping station may be hampered. It may also become difficult to fix a polder level that will meet the requirements of all kinds of soil.

CHEMICAL COMPOSITION OF SOIL

Chlorides

Through diffusion, the soil moisture of land covered with water has the same composition as the water on top. Thus in lakes in the interior, the soil does not contain salt. In areas reclaimed from the sea, however, the soil is saline. This salt consists of 85 per cent NaCl. As shown in table 1, the moisture content of the soil increases in proportion to the clay content; clay soils reclaimed from the sea, therefore, will contain more salt than the sandy soils. If the sea water has a concentration of 20 gm. of NaCl per liter, heavy clay soils will contain about 2 per cent NaCl, and sandy soils, 0.5 per cent.

TABLE 3
Salt content, in spring, of a soil reclaimed from the sea
In grams per liter soil moisture

LAYER, CM.	NaCl CONTENT				
	First year	1 year after ditching	2 years after ditching	3 years after ditching	4 years after ditching
<i>Sandy soil</i>					
0-5	12	1	1	1	
5-20	24	4	0	1	
20-50	21	15	1	1	
50-80	20	20	4	1	
<i>Clay soil</i>					
0-5	18	8	1	3	0
5-20	21	9	2	1	0
20-50	19	15	6	4	1
50-80	18	18	13	10	5

Under good drainage conditions, for example where field ditches are 10 to 20 m. apart, the wet Dutch climate will soon leach out the salt completely. This process is more rapid in sandy soils than in clay soils.

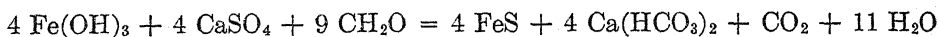
During summer there is a certain capillary rise of salt to the surface, but this rise is of little importance compared with the leaching during the winter months.

Table 3 gives some figures on the rapidity of desalinization. In the Netherlands the salt concentration of the soil moisture is often taken as a measure of the salinity of the soil. This concentration, used in table 3, has some advantages over the salt content per unit of dry matter (11). In the cases mentioned in table 3, the first winter after ditching was dry (150 mm. rainfall), the next, wet (348 mm.).

Cultivation need not be delayed until the soil is wholly free from salt. For planting, a concentration of 3 gm. NaCl per liter soil moisture in the topsoil is frequently adopted as a limit, though under favorable conditions a higher concentration is permissible.

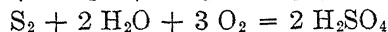
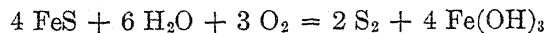
Sulfates

Before drainage, the soil is in an anaerobic condition. In this environment, sulfate-reducing bacteria oxidize the organic matter of the soil with the aid of the gypsum in the sea water. Thus sulfate is reduced to sulfide, which reacts with the iron in the soil. If the organic matter is designated as CH_2O , the equation is as follows:



Gradually a large part of the black FeS becomes FeS_2 , and elementary sulfur also is formed. Then the black color may disappear, as in old sea clay soils.

Thus, a large amount of sulfur accumulates in the soil. This accumulation is proportional to the clay and humus contents. After drainage, most of the pyrite oxidizes; the H_2SO_4 formed reacts with the CaCO_3 , and CaSO_4 is formed:



Such a large quantity of gypsum is formed that for some years the soil solution is saturated with gypsum. Even crystallized gypsum occurs in the soil. As the oxidation of pyrite is a gradual process, it takes about 6 years for the sulfate content of the topsoil moisture to drop below 0.7 gm. per liter, corresponding to 1 gm. gypsum per liter.

After drainage, disappearance of the black color of young silt soils is a good indication of the development of aerobic conditions in the profile. It takes about 4 years for this black color to disappear from the upper 50 cm.

Exchangeable bases

Because of saturation with sea water, the absorption complex of soil reclaimed from the sea contains a rather large amount of sodium. One might think that after drainage and leaching of the salt, soil structural difficulties would arise. But because of the large amount of gypsum formed after drainage, the concentration of salts in the soil moisture remains sufficiently high to keep the complex flocculated. Moreover, the CaSO_4 rapidly changes the sodium clay into calcium clay. Table 4 illustrates this change in a polder the soil moisture of which contained 22 gm. of NaCl per liter. Four years after ditching, the NaCl content had dropped to 2 gm.; and since the fifth year, the soil has been almost free from salt.

Of the Zuiderzee polders, only the first was reclaimed from salt water. When this polder was constructed, the Zuiderzee was still a salt water bay. To facilitate the formation of the other polders, however, this bay was cut off from the North Sea by means of a dam. The lake thus formed soon became a fresh water basin because of the inflow of rivers. At low tide the water of the lake can be drained into the North Sea through sluices in the dam. When the water of the lake had become fresh, the NaCl of the bottom diffused into the fresh water above. As a consequence, the equilibrium between the soil moisture and the absorption complex was upset.

As the soil contains CaCO_3 , which is slightly soluble, there is a tendency to replace the exchangeable sodium by calcium. The calcium, dissolved from the CaCO_3 , is fixed in the soil, and the exchanged sodium diffuses into the fresh water above as Na_2CO_3 . Thus the solution of CaCO_3 and the exchange of calcium for sodium continues. This process is promoted by the extreme fineness of the CaCO_3 and the abundance of water. Except for the first polder of the Zuiderzee, more than 10 years was available for this process. It is no wonder, then, that in the Noordoostpolder, which was created some years after the water of the lake had become fresh, the soil contained only a small quantity of exchangeable sodium.

TABLE 4
Exchangeable cations in the topsoil of a polder reclaimed from salt water

TIME	Ca	Mg	K	Na
	%	%	%	%
Just after draining	17	35	9	39
4 years after ditching	73	17	5	5
7 years after ditching	82	10	6	2
Final situation	87	8	4	1

SEEPAGE

As the water table in the polders lies several meters below that of the surrounding country, water tends to flow through the subsoil into the polder. This flow often takes place through the deeper subsoil, which in the Netherlands is usually composed of highly permeable sand of Pleistocene age (fig. 4).

Because of the high permeability of this deeper subsoil, the influx of seepage waters depends mainly on the thickness and permeability of the overlying Holocene layers. Usually these layers are partly composed of heavy clay, which is rather impermeable if it is uncracked, as is generally the case below $1\frac{1}{2}$ m. Then seepage is of little importance.

In polders where the Holocene layers are thin or even absent, seepage is stronger. It may be so strong that from an economical point of view it is impossible to drain the lake and keep it dry. In that case, the work has to be abandoned. Such a case actually occurred in the Netherlands.

In most polders, seepage amounts to 100 to 300 mm. a year. In some polders, however, this figure is as high as 15 mm. a day. All this water must be removed by pumps.

Seepage water does not rise with the same speed in all parts of the polder. Generally, seepage is especially great along the borders; moreover, it may occur in the central part in places where the covering layers have a higher permeability owing to sandy strips in the subsoil.

Most of the seepage water finally flows into the canals, but part of it comes to the surface in the fields. If seepage is small, only the processes of drying and ripening of the soil are hampered, and consequently the permeability of the soil remains low. When seepage is greater, much of the water is carried off by the tile drains. Seepage must be very great, however, before its agricultural conse-

quences get beyond the control of tile drain systems. In such cases, the soil is put under grass, which is not so sensitive to a high water table.

Sometimes seepage waters contain $\text{Fe}(\text{HCO}_3)_2$, which oxidizes in the tiles to $\text{Fe}(\text{OH})_3$. This compound is deposited in the tiles and often clogs them.

The greatest difficulties are caused by salt seepage waters. In normal soils, capillary rise is of little importance. In soils showing seepage, the capillary water movement, however, is maintained by the seepage water. If this is salt, so much salt may rise to the surface that it is no longer negligible as compared with the quantity that can be leached during the following winter. In such patches, desalinization is a slow process; in the worst cases, desalinization has still been incomplete 20 years after drainage.

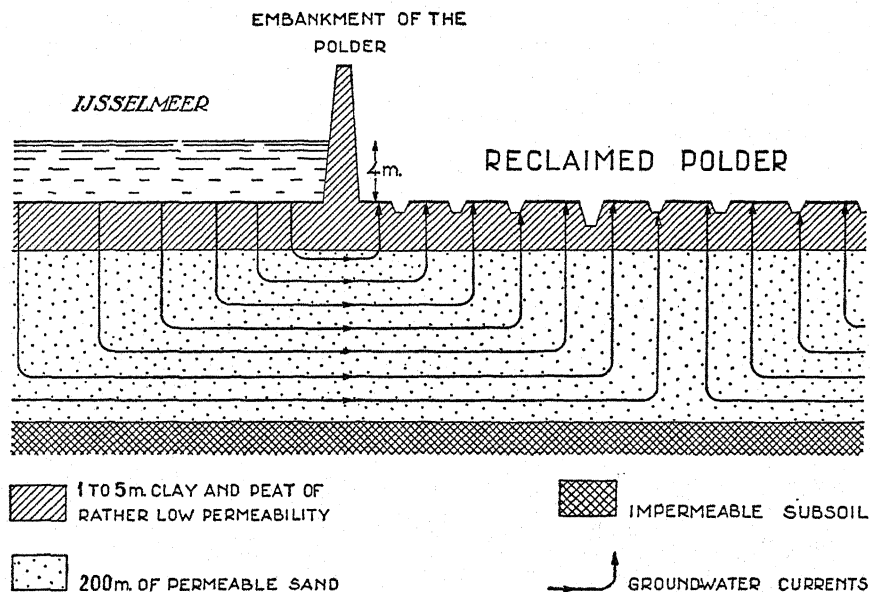


FIG. 4. SEEPAGE INTO THE ZUIDERZEE POLDERS

DITCHING AND TILING

The smallest units in a drainage system in a new polder are field ditches or tile drains. The construction of these small waterways is very important from the standpoint of soil science, as they promote drying of the soil indirectly by preventing formation of pools. From an agricultural standpoint they are indispensable to putting the polder under cultivation. This is readily understood in the case of a soil reclaimed from the sea. It is only after leaching of the salt, a process which requires good drainage, that planting becomes possible. For nonsaline soils, also, good drainage is important. In the beginning, the soils have a weak structure, and in case of excess water it very soon becomes impossible to travel over the land with implements. Moreover, in the beginning, the soil has a very low moisture-storing capacity. Pools are easily formed, causing a collapse of soil structure.

Because drainage by field ditches and tile drains is a very important part of the reclamation, many investigators have studied the subject of drainage and permeability of the polder soils (5, 8).

Because of labor shortages, it is impossible to provide tile drains immediately in a newly drained polder. Moreover, soil conditions often do not permit transport of heavy tiles. Therefore, after the excavation of canals and main ditches, digging of field ditches is the first operation. These field ditches have another advantage over tile drains: they allow the surface water to flow away rapidly and thus prevent formation of pools in the initial stage of reclamation when the soils still are low in permeability.

On sandy soils, the space between the field ditches varies from 8 to 50 m. according to the fineness of the sand and the thickness of the sandy layer. On soils with a clay content of 4 to 8 per cent, which are very low in permeability and will not improve by cracking, the distance between the field ditches is 8 m. A shorter distance would be desirable but not practical. As a rule, heavier soils are cracked to some extent by the time they are put under cultivation. In such soils a distance of 12 m. will suffice. Afterward, when the formation of cracks has advanced farther, the distance between the field ditches may be greater.

After some years, the field ditches are replaced by tile drains. Because of the continued increase in the permeability of heavier soils, the tile drains can be laid farther apart than the field ditches, sometimes at a distance of more than 30 m.

Lately, it has been possible to increase the distance between the tiles on the very impermeable soils with a clay content of 4 to 8 per cent. This may be done by breaking the soils to a depth of 80 cm. every 2 or 3 m. with a subsoiler. In such cases the distances between the tile drains may be increased from 8 to 12 or 16 m.

RECLAMATION OF THE NEW LAND

In the initial stage of the draining of a lake, pumping is very easy. As the level of the water sinks, however, the flow of water becomes more difficult. To improve this flow, the main canals are generally dredged before or during the pumping out of the water. During the last stages of the pumping, however, the main canals silt up and have to be redredged more than once. As the main canals are present from the beginning, the rain water, too, can flow from the surface, and in spring, when evaporation starts to exceed rainfall, the surface can dry rather quickly.

After drainage, the soil is entirely saturated with water and is so weak structurally that it is impassable, except in sandy parts. This condition prevails during the first winter. The next summer the top layer dries so thoroughly that it will support machinery mounted on caterpillars. Seepage areas, however, remain impassable.

Then the laying out of a drainage system is the first concern. Lateral canals and main ditches are dug by means of draglines, separating fields of 800 by 300 m. (fig. 3). These fields are further drained by ditches 60 cm. deep, which are dug with large plows.

If the soils are saline, 1 or 2 years should elapse between digging of the field

ditches and planting of a crop. Nonsaline soils can be planted immediately after ditching.

If planting is done shortly after drainage, it presents few difficulties, as the soil is still bare. Moreover, the uppermost layer has a crumbly structure and provides a good natural seedbed. The reclamation of larger areas is a time-consuming process, however, for it is usually impossible to reclaim more than 10,000 hectares a year. In the later stages, the soils that are not yet reclaimed become covered by a dense natural vegetation. In the Noordoostpolder a dense vegetation of reed (*Phragmites communis*) developed. Before a seedbed could be prepared, this vegetation had to be removed, then repeated plowing was necessary.

Other agricultural activities do not differ much from those followed on normal Dutch soils, although, because of labor shortages, the work is highly mechanized. Cereals occupy a prominent place in the crop rotation, and the growing of clovers is of great importance. The large number of field ditches presents a serious obstacle to farming. The ditches, therefore, are replaced by tile drains as soon as possible.

In addition to the construction of the drainage system, a large number of other operations must be carried out. The more extensive the area to be drained, the more urgent is the need for roads, farm sheds, and barracks for the laborers. All the work on smaller polders can be directed from the surrounding areas and a large part of the reclamation can be done by neighboring farmers. In the Zuiderzee polders, each with an area of 50,000 hectares, special provisions have to be made. In such cases, a special agency must be established for the reclamation work. This agency also directs the colonization, that is, the planning and construction of villages and farms, the leasing of land, and social organization. Such large-scale projects can be operated only by the government.

Putting sandy areas under cultivation presents a special problem. As flat sandy areas are subject to wind erosion, reclamation work is usually done during the rainy period, straw is used to prevent blowing, and the reclaimed sandy soils are put under grass.

In a polder, the clayey soils generally occupy the larger part. The level of the polder waters is, therefore, adapted to the requirements of these soils. Generally it lies more than 1 m. below the soil surface. At this level the moisture content of sandy soils is too low for good growth of crops, and the water table is raised artificially and maintained at a higher level through subirrigation (6). Water is let into the main ditches and penetrates the soil by way of the tile drains. As the polder surface lies at a lower level than the surrounding land, water can be easily drawn in. Of course, a system of ditches, sluices, and weirs is required to distribute the water and prevent a useless flow to the polder canals at a deeper level.

Once all the soil has been put under cultivation, the farms have been built, and the social organization of the polder is complete, the soil is leased to farmers. Each holding comprises 10 to 50 hectares, most commonly 24 to 36 hectares. Sandy soils are used mainly for grassland; the more clayey soils, for arable land. The latter soils are very fertile: a hectare will produce 4,000 kgm. of wheat, 4,000 kgm. of oats, 25,000 kgm. of potatoes, or 45,000 kgm. of sugar beets.

USE OF FERTILIZERS

As shown in table 1, the phosphorus content of sandy soils is so low that, from the very beginning, the phosphorus requirements of crops must be met through fertilization. On the heavier soils also, a small amount of phosphate is required. Sandy soils can do without potassium fertilizer for several years; the more clayey soils, for several centuries. Liming is unnecessary because of the high content of CaCO_3 . As a rule, no microelements are needed, though on very sandy soils in the Zuiderzee polders Mn deficiency was noted, and cattle, grazing on sandy grassland, in some areas showed symptoms of Cu and Co deficiencies.

The nitrogen economy of the drained soils is very complicated. On normal Dutch clay soils, formation and decomposition of organic matter are in equilibrium at a certain level, and therefore the humus content of a certain soil appears to be constant. The soil type determines the level of this "equilibrium humus content." Since the nitrogen content of the humus is nearly constant, humus need not be taken into account in considering the nitrogen balance. As to the other factors in this balance, there are gains due to the activity of *Azotobacter* and *Rhizobium* and losses due to leaching and cropping. The result is insufficient nitrogen for optimal plant growth. Nitrogen fertilization is therefore required. For wheat, the equivalent of 40 kgm. pure N per hectare is normally applied.

In younger soils the amount of nitrogen available for plants is smaller for several reasons. First, the number and the activity of the *Azotobacter* are lower. Second, nitrogen seems to become fixed in the soil in some way. Possibly, the initial nitrogen content of the humus is below normal, and decomposition may perhaps furnish less nitrogen than is required for the formation of new humus. It may also be that the humus originally present is very stable, so that formation of humus exceeds decomposition.

Unquestionably, the young soils have larger nitrogen requirements, for during the first years about 40 kgm. more N, in the form of NO_3 , must be applied for wheat than on the corresponding normal soils. Nitrate is far more effective than ammonium nitrogen.

The nitrogen requirements can be met by growing clovers, which supply an excess of nitrogen. Moreover, repeated growing and plowing under of clovers results in more normal soil conditions.

Not all young soils show nitrogen fixation. Some soils, in fact, produce a considerable amount of nitrates. This has been noted on soils recently deposited, where the organic matter is still fresh and readily decomposable. As a rule, these soils show a higher humus content than the "equilibrium" previously mentioned.

CAT CLAY

The young silt of the Zuiderzee polders and most of the old sea clay are rich in CaCO_3 . Some old sea clay soils, however, have lost their CaCO_3 or never possessed it. In these soils, sulfides have accumulated. The H_2SO_4 and FeSO_4 , formed by oxidation after drainage, cannot be neutralized by CaCO_3 , and the soils become extremely acid. Van Bemmelen (1) and Van der Spek (9) have done much detailed research on these acid, or cat clay, soils. The following comments are based on their investigations.

In these cat clay soils pH values of 1 or 2 occur, though values of 2 or 3 are more common. H_2SO_4 , FeSO_4 , and $\text{Fe}_2(\text{SO}_4)_3$ extract the exchangeable bases from the complex and also attack the clay fraction. As a result, $\text{Al}_2(\text{SO}_4)_3$ also appears in the solution. Moreover, hydrolysis of the $\text{Fe}_2(\text{SO}_4)_3$, a compound hydrolyzing at a lower pH than $\text{Al}_2(\text{SO}_4)_3$, occurs, and a lemon-colored basic iron sulfate is formed. This is deposited along cracks and root fissures. Initially, the basic iron sulfate contains a rather large amount of H_2SO_4 ; because of the continued hydrolysis, this amount decreases gradually to a proportion of 1 Fe_2O_3 :1.3 SO_3 . In this process large quantities of aluminum and iron compounds leach from the soils and are deposited in the ditches or in the tile drains.

Cat clay soils are so acid that no plants can grow on them, and polders in which this type of soil occurs over large areas give very poor yields initially. Huge quantities of lime are required for neutralization of the cat clay soils. It is best to apply this lime only after most of the soluble acid compounds have been leached out. Usually 30,000 kgm. of CaCO_3 is needed per hectare.

TABLE 5

*Number of microorganisms in saline and salt-free soils, as determined by the plate method**
In millions per gram of soil

SOIL CONDITION AFTER DRAINAGE	MICROORGANISMS						
	First year	1 year after drainage	2 years after drainage	3 years after drainage	4 years after drainage	5 years after drainage	8 years after drainage
Saline.....	0.04	0.3	9	25	31	39	46
Salt-free.....	1	11	20	45	70	80	80

* Method of Waksman.

In many places, the acid layers are thin and the subsoil contains CaCO_3 . It is possible, then, to neutralize the acid topsoil by mixing it with the calcareous subsoil.

If lime is not applied, the pH of the soil increases gradually as a result of continued leaching of acid compounds and absorption of basic cations from fertilizers. This makes possible some arable farming, though it may be poor.

BACTERIAL POPULATION

Before drainage, the soils of the polders have a bacterial flora the larger part of which is adapted to the prevailing anaerobic conditions. Bacteria of cultivated soils also appear in small numbers in the topsoil; in salt-free soils this number is larger than that in saline soils.

After drainage, the numbers of bacteria increase rapidly, as shown by the data of Harmsen (2) and Van Schreven (7), quoted in table 5. This table shows that the bacterial flora develops rapidly after drainage. In saline soils, development proceeds less rapidly than in salt-free soils; in the former, marked development begins only after most of the salt has been removed by leaching, usually in the third year after drainage. The number of bacteria present after 8 years is about the same as in comparable older soils.

Table 5 shows total bacterial numbers. Not all species, however, will develop equally rapidly. *Azotobacter*, for example, develops much more slowly than the other species. A special problem is presented by the Rhizobia. After drainage these bacteria usually are scarce, except in small polders and in the larger polders along the former coast. The *Rhizobium meliloti* group is virtually absent. Natural development proceeds so slowly that it is necessary to inoculate the seed of *Medicago sativa* and *M. lupulina*.

The *Rhizobium trifolii* and *R. leguminosarum* groups are present in such large numbers and spread so rapidly that, after 3 years, inoculation is no longer needed for clover and peas. For the first crop of alfalfa, however, inoculation is necessary even in later years.

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EMBANKMENT AND CULTIVATION OF MARINE FORELAND

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In the northern part of the Netherlands, shoreward of the Wadden Islands, and in the south, the area of large estuaries, sedimentation along the coast is a common feature. This deposition is due to the rather high clay content of the water, especially in stormy weather, and to the weakness of the currents at the height of spring tide. The origin of the sediments has not yet been determined.

The poldering of coastal accretions started about 1,000 years ago. This method of developing land was possible because the foreland builds up to a level somewhat above that of average high tide. Thus the new land could be easily drained at low tide by discharging excess rain water through sluices. The mean tidal amplitude varies from about 150 to about 280 cm. in the Wadden area and from about 150 to about 400 cm. in the estuary region.

Formerly the embanking was done by individual farmers who had acquired property rights to the foreland bordering on their farms. Nowadays, nearly all parts of the coast where land buildup may be expected are owned by the state, and poldering is a state enterprise.

MORPHOLOGY

There is marked difference between the accretions in the south and the forelands in Groningen. In the south, in the Province of Zeeland, sedimentation takes place naturally on those spots where the clay content of the water is sufficient and the water quiets down at high tide. The forelands in Zeeland, locally called *schorren*, are traversed irregularly by creeks bordered by levees. The levee soils are sandier than the basins, which are farther from the creeks. Thus the foreland soils may form an intricate pattern of heavy and light soils.

In Groningen, where the foreland is called *kwelder*, the accretion of land is artificially accelerated. Squares of 16 hectares are laid out along the coast by means of small dams (fig. 1). In the basins thus formed, the water quiets at the turn of high tide and the clay particles settle. An extensive system of small ditches ensures rapid evacuation of the water after high tide and consequent drying of the freshly deposited sea mud. This protects the mud against scouring action during the next high tide. The small ditches are filled rapidly and have to be cleaned out a few times a year. This work is costly because of the labor involved, but nowadays, the small ditches are dug and cleaned mechanically.

In many places, the foreland slopes gently toward the coast; in other places, the reverse is true. The direction of the slope depends on the process of formation and on the age of the foreland.

VEGETATION

The flora of the lowest bare mud consists entirely of a film of algae. The next belt offers a good environment for *Salicornia herbacea*, though this halophyte

¹ Research Department, Noordoostpolder Authority.

often does not form a continuous cover. When the foreland has built up to such a level that flooding occurs only at spring tide, *Puccinellia* spp. become dominant. On the highest spots is found a vegetation mosaic in which *Obione portulacoides*, *Triticum litorale*, *Artemisia maritima*, or *Festuca rubra* may be dominant.

In 1924, *Spartina Townsendii* was imported into the Netherlands from southern England. It often forms a continuous cover in the *Salicornia* zone and grows readily about 20 cm. above low tide level, where it promotes sedimentation of clay through its rapid growth and rich foliage. *Spartina* has spread rapidly since 1924 and is now common in Zeeland.

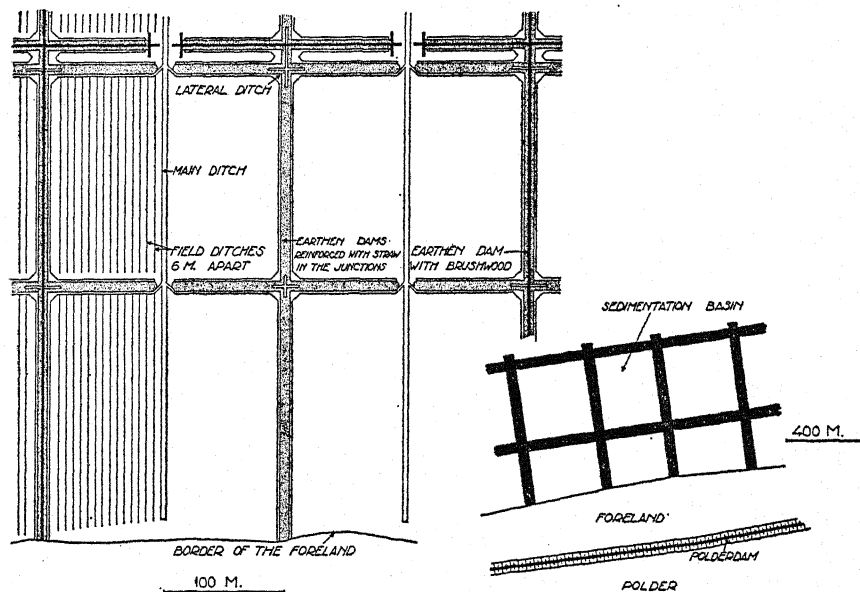


FIG. 1. SEDIMENTATION BASINS ALONG THE COAST IN THE NORTH OF THE NETHERLANDS

On the high forelands in the brackish regions, *Phragmites communis* sometimes forms a dense vegetation.

SOIL CONDITIONS

Nearly everywhere in the foreland the clay content of the soil diminishes with increasing depth. In some spots this transition is very gradual; elsewhere there is a sharp boundary between clay or clay loam and the underlying sand. If such a boundary occurs high in the profile, it forms a serious obstacle to the root systems of agricultural crops, particularly in soils with a coarse subsoil. The origin of these profiles is clear, because there is a close negative correlation between the level of the forelands and the rapidity with which the water runs over them. Because of this correlation, the deposition of clay particles increases with the growth of the foreland. Usually the clay content of the soil and the thickness of the clay cover

increase in the direction of the old coast. In these young marine clay soils two thirds of the $<16 \mu$ fraction consists of $<2 \mu$ particles.

The content of organic matter shows a positive correlation with the clay content, the former being nearly 10 per cent of the latter (fig. 2). After embankment and subsequent cultivation of the forelands, the organic matter content decreases to a rather constant level, nearly independent of the clay content.

The CaCO_3 content also is correlated with the clay content (fig. 2), but with the same clay content the amount of CaCO_3 decreases from south to north.

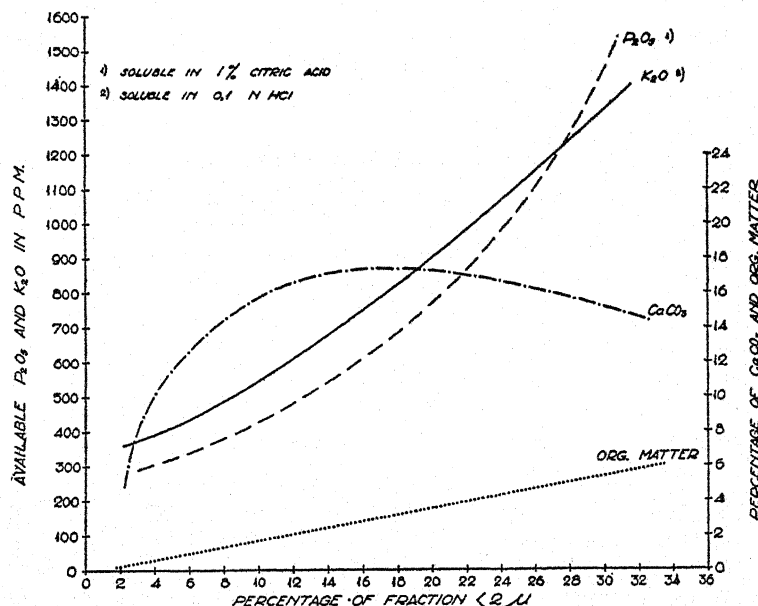


FIG. 2. RELATION BETWEEN CLAY CONTENT AND SOME OTHER SOIL CONSTITUENTS IN THE TOPSOIL OF MARINE FORELANDS IN THE SOUTH OF THE NETHERLANDS

The amounts of available K and PO_4 are rather high and likewise depend on the clay content (fig. 2). On old and high forelands, however, the amount of available PO_4 may decrease before poldering.

The permeability of the bare mud is nearly zero. That of a kwelder covered with vegetation is usually very high in the topsoil, especially in the heavy clay soils, but decreases with increasing depth.

EMBANKMENT

When the accretions have almost reached their ultimate level and the surface of the kwelder has become large enough, embankment can be carried out. If possible, the dam is built somewhat back from the edge of the kwelder so that some foreland clay remains available for repairing damage caused by storms. A sluice is built in the dam to discharge excess water. Behind the sluice, a basin

may be constructed which is filled at high tide and emptied suddenly at low tide to scour the mud out of the creek in front of the sluice.

A new polder commonly deprives some older polders of their outlets. Then the water of the hinterland must be evacuated through the new polder. In that case, the water courses and the new sluice must be built much larger than is required by the newly dammed polder. So as not to hamper the discharge of water from the rearland, the sluice and the main canal must be finished at the same time as the dam. Afterward the secondary ditches are dug, and the roads, connected with those in the hinterland, are constructed.

These embanked kwelders sometimes create serious difficulties in community planning. This is especially true in the Wadden area, where the land has been extended several times with narrow strips, without the establishment of a sufficient number of villages. Today, the settlement policy of a foreland polder and its relation to the environment are important subjects of research.

CULTIVATION

After the dam has been built, the soil must be put under cultivation. The broad creeks are filled with soil dug from the ditches, but most of the main creeks remain and are incorporated in the drainage system of the young polder. The smaller creeks are filled by plowing or are leveled with a bulldozer. This leveling must be done carefully to keep the sod on top of the profile. Formerly, the creeks were filled gradually; nowadays, the creeks sometimes are filled at once, since modern agriculture requires a rather flat surface.

In former times, soil tillage was very simple. Every second furrow was plowed very shallow. The first crop nearly always grew either in the furrows or on the bars. At present, tillage, like the breaking up of meadows, is very intensive and consists of plowing, discing, and harrowing. The depth of tillage is still no more than 7 to 8 cm., as the subsoil coming into the furrow slice may cause puddling. The *Spartina* vegetation, formerly unknown, as well as the *Triticum litorale* cover, must be mowed and burned before tillage.

If necessary, some field ditches (about 50 cm. wide and 30 cm. deep) are dug to promote desalinization and maintain a sufficiently low water table in winter during the first years. On old and high kwelders, the rains of a single winter may wash out enough salt to warrant planting of the land. Generally, the embankment of some bare mud or sand is unavoidable. Cultivation of such soils is very similar to that of soils formed on lake and sea bottoms.

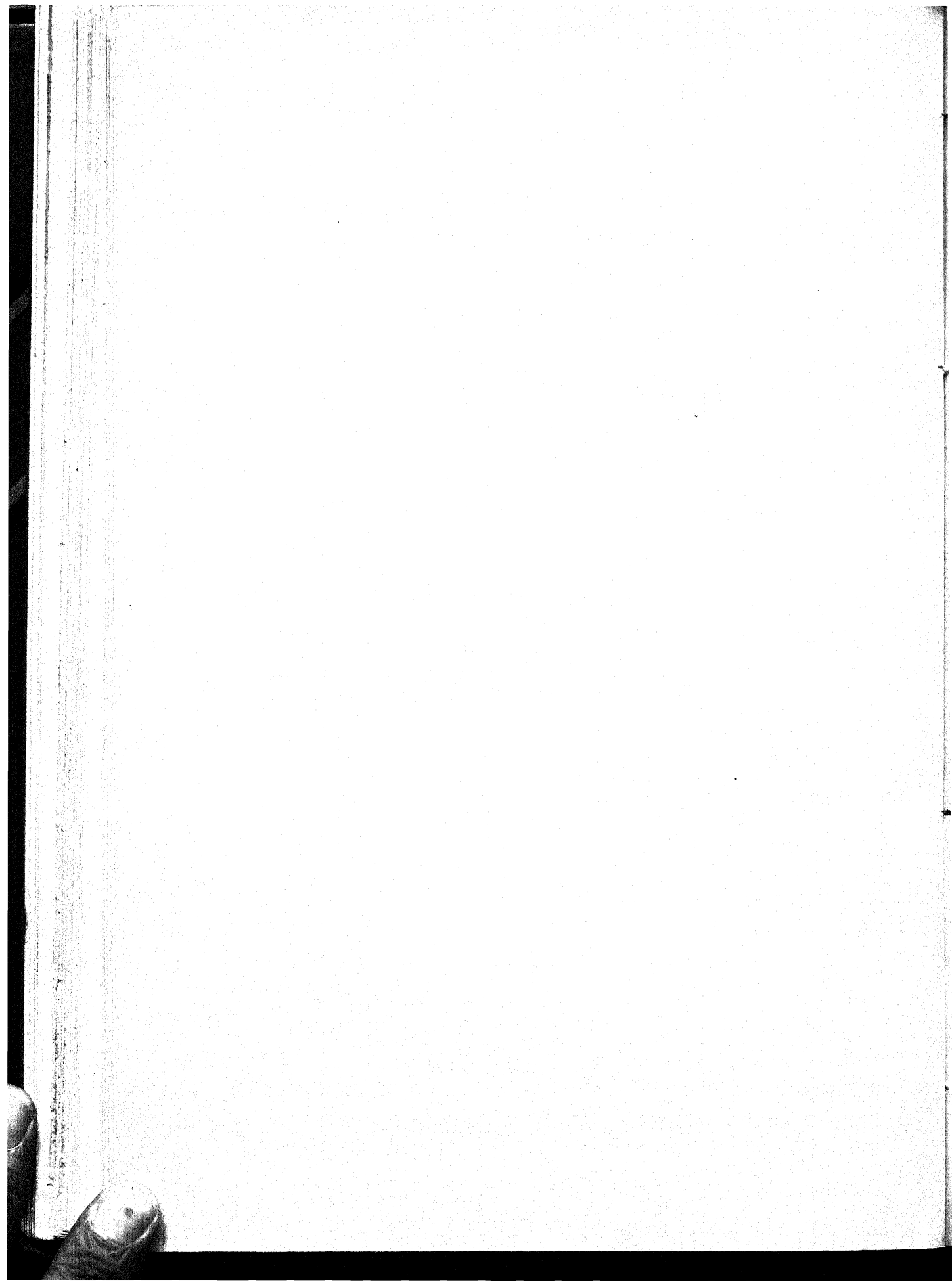
AGRICULTURE IN THE YOUNG POLDERS

Planting in the year of embankment is seldom possible, as the excess salt must first be washed out by rain. In the second summer, *Brassica Napus* is sown. This crop is grown for a second year, after which nearly all crops suited to Dutch marine clay soils can be grown.

In the first 5 to 10 years, the soil is readily worked. The sugar beet is a favorite crop. Cereals are subject to lodging because of the large quantities of N released by the decomposing sod.

In foreland with a high clay content, phosphate fertilizers are rarely needed for the first 10 to 20 years, and potash can be omitted for centuries. Forelands with a thin clay cover or a very low clay content and embanked sandbars are of much lower value.

Embankment as a means of gradually building up land is less spectacular than the pumping of large lakes or the reclamation of vast heath regions. Moreover, it is rather costly, if the accretion must be promoted by man. Since 1200, however, the Dutch have enlarged their country bit by bit with 233,000 hectares of former foreland, most of the area thus developed being excellent arable soil.



PHYSICAL PLANNING IN RECLAIMED AND NEWLY COLONIZED AREAS

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"The Lord created the world; the Dutch created their own country." This adage is well known all over the world. Today the Dutch still create. The difference between past and present creation lies in the way in which the new areas are reclaimed.

PLANNING IN EARLY RECLAMATION PROJECTS

Even before 1300 some land had been reclaimed. But about the year 1500, the Dutch became conspicuously successful in gaining land; from then on, the gains exceeded the losses. In the 17th century, merchants, who became wealthy by sending their ships to the East Indies, took the initiative in draining great parts of the area we now call the Province of Northern Holland. Draining in those years was an adventure, and in many cases, the societies of merchants and burgomasters lost the money they invested in the enterprise.

The newly formed land was wet. There were no roads. Knowledge of the soil was superficial. Perhaps the soil contained salt and therefore provided many surprises for the first farmers. The sad experiences in agriculture were summarized in the old saying: "The first farmer dies, the second suffers bitterly, the third has his bread." People also said: "They are winning the land for the third hand."

Up to the middle of the 19th century, the responsibility of the state was thought to be restricted to general adjustments to defend the land and the nation. These state adjustments were passive and contained no elements of planning. Private enterprise undoubtedly managed to create some prosperous areas, where farmers and others who made their living indirectly from the land were well-to-do people with a rather high cultural level. The present state of affairs, however, in areas such as the Haarlemmermeer and the Anna Paulowna polder, which were drained in 1852, must not mislead us about the merits of the colonization methods of former times. During the first years after reclamation of the polders and heaths the ruling factor was the struggle for life. Planning, as such, was unknown. The first farmers were exposed to all sorts of diseases and had no access to medical care; therefore, the death rate was exorbitantly high. Farming involved great risks in the newly cultivated areas, and many pioneers could not endure the economic, physical, and moral hardships of the first 10 or 12 years. In the struggle for life, the fittest survived, in line with the Darwinian theory.

In Holland today it is a common conviction, not influenced by political thinking but based on past experience, that the risks of the first years are too great to be borne by private enterprise. The State of the Netherlands, therefore, is playing a prominent part in the reclamation of the new land in the Zuiderzee.

Physical planning from the early days to the end of the 19th century was very

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simple. One thing that had to be done was parceling the land. Each shareholder in any company founded to reclaim one of the numerous lakes in the Low Countries after drainage had to be content with a definite part of the land. In the Netherlands, moreover, ditches had to be dug and roads built. The result was a rectangular-patterned land, very easily recognized on the maps. No attention was paid to the aesthetic effect of the landscape. No careful study was made of arteries of communication with the *old land* (as people in Holland say), nor was any attempt made to locate the villages efficiently. The types of farmhouses built in the new land varied greatly, and a hodge-podge of architectural styles met the eye.

In contrast with ideas about reclamation in the Netherlands today, everything was left to private initiative. An over-all picture was entirely lacking. Society and the frame in which it could develop grew spontaneously and led to conspicuous faults: lack of efficient dispersion of villages and other settlements; poor distribution of stores for the inhabitants; endless rows of dwellings along the roads, resulting in high costs of distributing goods and making a stereotyped and ugly landscape; poorly drawn community frontiers.

DEVELOPMENT OF PHYSICAL PLANNING

Physical planning started in the towns. It was called *stedebouw* in Dutch and meant the building of cities or city development. At first, only technical and social-hygienic factors received attention. City development in the beginning was not based on serious economic and social research. Not until 1930 were broader surveys made in the Netherlands, and the first of these were in Amsterdam and other large cities. Rural planning came later.

From the time physical planning became associated with social research not only was its function broadened beyond that of a mere technical operation, but it became interwoven with elements of social planning. This is very clear in the plans made for the Zuiderzee polders.

The Zuiderzee polders provide ideal opportunities for physical planning. The drawbacks that normally make it impossible to solve traffic problems or to locate buildings in the right spot are absent in the new land. The planners took advantage of the opportunities offered here. In the first Zuiderzee polder, the Wieringermeer, planning was still primitive though much better than in the Haarlemmermeer. In the second polder of the Zuiderzee reclamation, the Noord-oostpolder, the planning is being done by team work. Students in agricultural sciences, hydrological experts, sociologists and economists, administrators, and architects are working here in close cooperation.

The development of physical planning is revealed in the Zuiderzee polders. Nowhere in the Netherlands could planning—physical planning associated with social and economic planning—be realized more perfectly. Here planning became, in the true sense, building a new community.

PURPOSES IN PLANNING THE ZUIDERZEE POLDERS

The ends pursued in the Zuiderzee polders are threefold: first, to create a rural area comprising farms of an economical size; second, to create a *country-*

side, in the Dutch sense of the word; third, to create a satisfactory landscape by harmoniously uniting economy and aesthetics.

As to the first purpose of polder planning, the goal of the reclamation was to provide fertile soils, and therefore the shape of the polders had to be determined on the basis of sufficient knowledge of the soil. There is no sense in enclosing and draining infertile soils. The knowledge gathered by state scientists will safeguard the first farmers from suffering as a result of lack of practical experience. A group of research workers examines the soils after drainage and determines the need for fertilizers or manure and the possibilities of mechanization for farms of different sizes. Data have been collected on the yield per hectare during the first years. The principles of land division are wholly rational. The rectangular shape of the parcels stimulates mechanization. Careful attention is paid to the building of farmhouses. The state, the sole owner of the reclaimed land, also builds the farmsteads, which must be practical and yet meet aesthetic standards. Much care is given to the selection of the colonists. After 3 or 4 years of state management, normal private management is introduced. The future tenants are chosen from a great number of applicants. The state demands three qualifications of these applicants: skill, financial stability, and the mentality of the real pioneer in new circumstances. State officials select the farmers and have a hand also in selecting the farmhands.

In the Noordoostpolder, where the most modern ideas of planning prevail and where the mutual relationships of all aspects of planning are taken into account, the size of the farms will vary from about 12 to 48 hectares, with an average of 24 hectares, in accordance with the standard parcel of this size (300 by 800 m.). The average farm in Holland is considerably smaller than this. To the Dutch, a 48-hectare farm is large; a 100-hectare farm is huge. Seventy per cent of the farms do not exceed 10 hectares. These are intensive family-size farms. In the Zuiderzee polders a large number of farmers employ farmhands. An important improvement over the old land is that in the new land the grounds belonging to one farm are in one piece.

In the Noordoostpolder, the aspirant-farmers have seen the profits of mechanization by working for the temporary government management for a few months or even several years. Draglines are used for digging broad ditches, ditch plows for the smaller ones, bulldozers for spreading the earth thrown out of the ditches, and tractors for pulling broad harrows, binders, and combines. The mechanical equipment of the state management saves labor on a large scale. The private tenant naturally will try to lower his labor costs by introducing the labor-saving machines he has seen in operation. He has become machine-minded. It may be necessary for him to use these implements cooperatively with his neighbors. To facilitate this form of cooperation, the planners in the Noordoostpolder have seen to it that farms of the same size, and therefore of the same sort of management, are grouped together.

The planned distribution of farms as to size is therefore not irregular in the Noordoostpolder. There is some system to it. Another element in this distribution of farms is their location with regard to the villages. So far as possible, the principle is maintained of planning the smaller farms, of 10 to 12 hectares, in the

immediate neighborhood of the villages to enable the tenants and their families to visit these villages readily. In the Netherlands the tenant or owner of a small holding has no car. From experience in old areas, it is expected that the small farms will be managed more intensively, thus requiring a larger labor force per hectare. By placing the smaller farms around the villages, the planners ensure that the greatest possible number of rural people will profit from the services of these near-by villages. Moreover, the clusters of smaller farms adjoining the villages can mutually develop an economic and cultural style of their own. Development of a specific economic style is necessary to avoid a breakdown. Sociologically, this means that the individuals can attain this end only by acting as a group. Here, very clearly, physical and social planning are interwoven.

The second purpose of planning in the polders, creation of an ideal Dutch *countryside* is based on the existence in Holland of many villages of 500 to 1,500 inhabitants, situated at distances varying from 3 to 6 km. In the Wieringermeer, these distances are about 5 km. In the Noordoostpolder they are 6 to 7 km. Great care has been taken to locate the villages in the Noordoostpolder at distances fitting the existing conditions of rural work and life. The task of the planners is to make the Dutch countryside. The farmhand living in a village should not have to travel far to the farm on which he works. The farmer's children should not have to walk more than half an hour to attend the village school. The housewife who wants to do her shopping in the village should be able to reach the grocer's or the butcher's, the drugstore or the baker's shop, in 10 minutes by bicycle. The distances pointed out for the Noordoostpolder meet the demands of rural life in Holland. The distances in the Wieringermeer are too short.

Planning in Dutch rural areas is based on the use of bicycles, not cars. It is possible, however, that the rapid increase in the number of bicycles equipped with small motors will change the situation. Physical planning is a dynamic activity. Except for this possibility of change, the network of roads in the Noordoostpolder meets the demands of the rural people for short distances, and cycling paths have been planned to shorten the distances still more.

There are no farmhouses or barns in the villages. The farmer lives on his land. The village people consist of farmhands, storekeepers, postmen, schoolmasters, and clergymen. Only the group called *the first farmhands*, who are permanently connected with one particular farm, will be settled in the neighborhood of the farmhouses.

All the villages are built according to a plan, both in the Wieringermeer and the Noordoostpolder. In future polders, this will be true also. These plans include streets, houses, official buildings, and shops. For each village, a little park is planned for recreation and as a wind shelter. Incidentally, it is a great pity that through the wanton inundation of the Wieringermeer by the Germans a fortnight before their official capitulation, the parks in the neighborhood of the villages in that polder were destroyed.

In the Wieringermeer, the villages are the largest settlements. A regional town would have no function in this small polder of about 200 sq. km. The Noordoostpolder, on the other hand, covers an area of nearly 500 sq. km. In its center a capital, Emmeloord, was laid out. This, it is anticipated, will eventually have

8,000 to 10,000 inhabitants. Comparative studies led to the belief that the Noordoostpolder, because of its size and the density of its population, should have its own regional town, with larger stores, offices, and high schools, which would serve the surrounding villages and scattered farms. Perhaps some industries will settle here. A railway station is planned, despite many uncertainties.

Roads and canals in the Noordoostpolder lead to the capital. Naturally, the canals also serve for drainage as well as for transportation. Emmeloord is planned like the hub of a wheel. The executive board of the polder stimulates the development of the capital to serve as a regional center, the nucleus of interests, the place where farmers of the whole area will meet. Today, Emmeloord is under construction. At the moment, only a few of the outskirts have been completed, but the heart of the town is growing steadily. A plan based on a detailed analysis of the function of the town has, however, been completed.

In the Zuiderzee polders the farm size is greater, the distances from village to village and from farm to village are longer, the land division is much better, and the population is much less dense than in comparable areas of old rural Holland. In fact, no strong population pressure in the polders is anticipated for several decades. No revolutionary changes in the countryside are involved in the new scheme. The work carried on by the State of the Netherlands is very important, but there is no desire for an overcentralized government. The object is to create farms run by private individuals. The continuation of some government farms is accounted for by the desire to obtain standards for the fixing of prices of agricultural products and rents and for the making of experiments. Many measures taken by the executive board, which seem far-reaching, are temporary.

The third end of polder planning, creation of a satisfactory landscape, is obvious in the Noordoostpolder. An area of nearly 500 sq. km. of flat land is too immense for the human eye. It is thought necessary to subdivide the area and to build horizons. The roadsides, therefore, will be planted with shade trees; in fact, some have already been planted. These plantings will follow a definite plan, the purpose of which is to bring about an orderly division of the vast area. In addition, three woods covering several square kilometers each will be planted on soils least suited to agriculture. The planting of trees has a practical as well as an aesthetic value. To cyclists, especially farmhands and school children, the trees will be very useful in providing some protection from the wind, which in this flat land is very strong.

In short, physical planning is an instrument by which the best use is made of available land in the interests of the community as a whole. Creating a polder is a problem not only in hydrologic science and agriculture but also in rural planning. Social scientists have examined the rural social structure and have given advice on the building of villages. In their rural sociological studies, they have also had recourse to the wisdom of farmers and farmhands in deciding how to build up a rural community that will provide the framework of a happy family life. One of the striking features in the planning of the Zuiderzee polders is the cooperation of all sorts of experts. In rural planning today, the study of the individual and of society is as important as the study of soils or harmful insects.

SOIL SCIENCE

VOLUME 74

August 1952

NUMBER 2

CATION-EXCHANGE EQUILIBRIA ON CLAY MINERALS

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Received for publication August 21, 1951

The purpose of the present paper is to compare various cation-exchange equations derived by regarding the exchanger phase + solution phase as a Donnan system with various equations that have been proposed. A theoretical treatment is given also for the case where the exchanger phase consists of, for instance, a comparatively dilute montmorillonite suspension, where the exchangeable ions form a swarm or so-called diffuse double layer around each particle.

HOMOVALENT EXCHANGE

In homovalent exchange all the various exchange equations agree, and for K^+ and Na^+ , for instance, the equilibrium condition can be formulated

$$\frac{[K] (Na)}{(K) [Na]} = K \quad (1)$$

in which the brackets refer to amounts present in the exchanger phase as exchangeable ions, and the parentheses denote the activities of the ions in the solution.

Approaches to the problem of homovalent exchange leading to equation (1) have been different.

Jenny (5) started from statistical considerations, interpreting the constant K as the ratio of the "oscillation volumes" of the two ions in question. He pictured the exchangeable ions as held rather closely to the fixed charges of the exchanger and oscillating in a definite space around each charge. This model is therefore not compatible with the concept of a diffuse double layer.

Vanselow (12) derived his equation by regarding the exchanger with its ions as a mix-crystal or, better, a solid solution. If the exchanger charges are denoted by Z , then in the case of Na^+ and K^+ as exchangeable ions, NaZ and KZ form a solid solution. The activity of NaZ and KZ is thus given by their mole fraction, as for an ideal solid solution. The constant K must here be interpreted as the ratio of the solubility products of NaZ and KZ respectively in their pure states. As Z^- can hardly exist in the solution, the similarity between the exchanger $(Na,K)Z$ and a solid solution is only formal. Nevertheless, Vanselow's approach to the problem is interesting.

The approach of Krishnamoorthy and Overstreet (6) is in principle the same as that of Vanselow, although the mole fraction of these workers in the pres-

ence of polyvalent ions is somewhat modified. Krishnamoorthy and Overstreet also assume a relatively homogenous exchanger phase which is not compatible with a diffuse double layer.

When the exchange process is interpreted as a redistribution of ions in a Donnan system, the equilibrium constant K in equation (1) is the ratio of the activity coefficients of Na and K in the exchanger phase. Even if the exchanger phase is nonuniform electrically, because of formation of diffuse double layers, the equation applies equally well.

There are too many approximations involved for K to be perfectly constant. In particular, K is likely to vary with varying proportions of the ions concerned in cases where the exchanger phase is nonuniform with respect to the specific interaction of the ions and exchange material. For a more uniform exchange material it seems to be relatively constant and is of great value as a characteristic for such a material.

HETEROVALENT EXCHANGE

The equations of interest in heterovalent exchange are those of Vanselow (12) and of Krishnamoorthy and Overstreet (6), which will be discussed in connection with the question based on the Donnan theory. In the case of Na and Ca, for example, the common formulation of the equilibrium equation for a Donnan system reads

$$\frac{(\text{Na})_i^2 (\text{Ca})_o}{(\text{Na})_o^2 (\text{Ca})_i} = 1$$

where o and i refer to the solution and exchanger phase respectively. The exchanger phase is here supposed to contain a certain amount of negative charges which for some reason are unable to diffuse out of the phase. These charges are supposed to occupy a definite volume V in the exchanger phase and are further supposed to be uniformly distributed in this volume. The activities of the ions in the exchanger phase can then be written as the amount of these ions in the phase divided by the volume V and multiplied by an activity coefficient f . In this way,

$$\frac{[\text{Na}]^2 (\text{Ca})}{(\text{Na})^2 [\text{Ca}] V} = \frac{f_{\text{Ca}}}{f_{\text{Na}}^2} = K \quad (2)$$

is obtained, the brackets and parentheses having the significance mentioned earlier. The amounts in the brackets are, of course, not entirely exchangeable ions, that is, they do not all belong to the negative nondiffusible charges of the exchanger phase; the negative ions in the solution have also a tendency to diffuse into the exchanger phase accompanied by cations. According to the Donnan theory the concentration of these negative ions in the exchanger phase must always be less than in the solution and, if the concentration of negative nondiffusible charges in the exchanger phase is great compared to the concentration of negative ions in the solution, then the concentration of diffusible negative ions in the exchanger can, for all practical purposes, be neglected. The

amounts in the brackets can then be regarded as purely exchangeable ions belonging only to the negative nondiffusible charges of the exchanger phase. Equation (2) can, however, be changed into another form. If X is the charge concentration in the volume V of the exchanger phase, then $V \cdot X$ is the sum of all cations (in equivalents) in the phase, and VX can be expressed by

$$V \cdot X = [\text{Na}] + 2[\text{Ca}] = [\text{Na} + 2\text{Ca}] \quad (3)$$

where the quantities of Na^+ and Ca^{++} are expressed in moles. If V is solved from equation (3) and substituted in (2), this takes the form

$$\frac{[\text{Na}]^2 \cdot (\text{Ca}) \cdot X}{(\text{Na})^2 [\text{Ca}] [\text{Na} + 2\text{Ca}]} = K \quad (4)$$

If ions other than Na^+ and Ca^{++} are also present, they have to be included in the summation term in the denominator.

For the same system the equation of Vanselow reads

$$\frac{[\text{Na}]^2 (\text{Ca})}{(\text{Na})^2 [\text{Ca}] [\text{Na} + \text{Ca}]} = K \quad (5)$$

and that of Krishnamoorthy and Overstreet

$$\frac{[\text{Na}]^2 (\text{Ca})}{(\text{Na})^2 [\text{Ca}] [\text{Na} + 1.5 \text{Ca}]} = K \quad (6)$$

The main difference between equation (4) and equations (5) and (6) is that in (4) the charge concentration X appears in the numerator. Since X is a constant quantity it does not influence the constancy of K , but its presence in the equation constitutes an important difference in principle which will be discussed later. The remaining difference between the equations lies in the factor for Ca in the summation term in the denominator. In practice this difference is of but little importance, as it is difficult to decide, without extensive experimental evidence, whether the choice of 1.5 in equation (6) is justified as compared with 2 in equation (4). It is by no means certain that the specific interaction of the ions in question with the surface (or probably, better, with the structure of the adsorbed water at the surfaces) is independent of the relative amounts of ions present. This may change the constant K in such a direction that the choice of the factor 1.5 merely counteracts this change. The experimental data given by Krishnamoorthy and Overstreet (7) seem to favor equation (6) rather than (4) and (5), but their experiments were done with monovalent ions of rather strong exchanging properties (that is, with relatively low activity coefficients in the exchange phase). Their choice of the factor 1.5, which is based on statistical considerations, implies that all the exchangeable cations are held very close to the fixed charges at the surface, a condition which may be questioned.

With regard to Vanselow's equation, the factor 1 for Ca in the summation term implies that 1 mole of CaZ_2 has the same volume as one mole of NaZ , which is obviously impossible. (In his case NaZ and CaZ_2 are supposed to form

an ideal solid solution.) A more reasonable assumption is that one mole of NaZ and half a mole of CaZ_2 occupy the same volume, which immediately leads to a factor of 2 for Ca as in equation (4).

The significance of X , the charge concentration in the exchange phase, in equation (4) requires further discussion. It is, of course, difficult to estimate X , but in the case of exchangers of the same class, such as clay minerals, it can be taken to be proportional to the exchange capacity of the material in question. A modified equation containing the exchange capacity C of the exchanger can thus be written

$$\frac{[\text{Na}]^2(\text{Ca}) \cdot C}{(\text{Na})^2[\text{Ca}][\text{Na} + 2\text{Ca}]} = K \quad (7)$$

Krishnamoorthy and Overstreet (7) have given the constant K according to their equation for the exchange equilibrium between H_4N^+ and Ca^{++} for a number of exchange materials. It is possible to calculate from their data the exchange capacity of all but one (Hanford clay) of the materials they used. From this a new constant can be obtained by multiplying their constant with the appropriate exchange capacity. Except for minor differences due to their factor 1.5 for Ca in the summation term, the resulting constant then corresponds to K in equation (7). The results of this calculation are as follows:

EXCHANGE MATERIAL	CLASS	EXCHANGE CAPACITY C IN ME./GM.	K ACCORDING TO K & O (7)	$K \cdot C$
Utah bentonite	Aluminum silicate	1.30	0.044	0.057
Yolo clay	Aluminum silicate	0.60	0.090	0.054
Aiken clay	Aluminum silicate	0.30	0.184	0.055
IR 100	Resin	1.72	0.0070	0.012
Ion X	Resin	4.20	0.0026	0.011

Yolo clay is of the montmorillonitic type and Aiken clay of the kaolinitic type. It is very interesting to note that $K \cdot C$ for the three clays is nearly the same; interpreted on the basis of equation (4), this means that the ratio of the activity coefficients of Ca^{++} and H_4N^+ is virtually the same for the three materials. This is also true for the two resinous exchangers. The results strongly support the principle underlying equation (4) and they also indicate that too much importance has been attached to the supposed differences in specific interaction of ions of different valency with different clay minerals. The great differences in K in the calculations are most probably mainly nonspecific for the ions, and depend almost entirely on the differences in the charge densities of the minerals. This is an important point which has been stressed by Mattson and co-workers (8, 9, 14) in several papers but which, with few exceptions, has received little attention.

It is rather surprising that a theory such as that underlying equation (4), based on so many approximations, should give such a satisfactory interpretation of experimental data as that shown in the foregoing calculations. Equation (4)

differs from (5) and (6) with respect to X because of the difference in the convention adopted when the equations were derived. In equation (4) the exchanger phase is treated in the same way as the solution phase, the concentration of the ions being expressed in the same way as in the solution. In equations (5) and (6) the convention adopted for the exchanger phase differs from that adopted for the solution. The activities of NaZ and CaZ_2 in their pure state are taken as unity, independent of their molar volumes; in principle this is the same as taking X equal to unity in equation (4). Thermodynamically it is unimportant what convention is used, but from the point of view of interpreting experimental results it may be very important. The data quoted in this paper are in favor of the convention adopted for describing Donnan equilibria.

Another interesting difference in principle between equation (4) and equations (5) and (6) is that more approximations are made in deriving (4) than in deriving (5) and (6). This should not be taken as unfavorable for (4); it arises from the fact that the assumptions underlying (5) and (6) have made certain approximations unnecessary.

HETEROVALENT EQUILIBRIA IN DIFFUSE DOUBLE LAYER SYSTEMS

The experiments referred to in the preceding section were all carried out with relatively high salt concentrations in the solution phase and with the colloid phase rather concentrated by centrifuging. These circumstances make the approximations less serious, since the diffuse double layer under these conditions should, theoretically, be of less importance.

It is of interest to compare the differences between an ideal Donnan system and a system in which the colloidal phase is made up of platelike, well-separated clay mineral particles, for instance montmorillonite, in equilibrium with a solution of monovalent and divalent cations. An equation based on the Poisson-Boltzmann differential equation has therefore been derived, showing the proportion of monovalent to total ions (in equivalents) in the diffuse double layer. For obvious reasons the derivation has been made for an ideal system, that is, one in which the activities of the ions are equal to their concentrations. This is, of course, an approximation, but nevertheless, the equation may still give some valuable information.

The Poisson-Boltzmann differential equation has been used with success for deriving a number of relationships in the colloid chemistry of charged surfaces (1, 2, 3, 4, 10, 11, 13). In connection with cation-exchange equilibria, it is used here to describe the electric field in the diffuse double layer as a function of the potential. By application of Boltzmann's principle and integration, a relatively simple equation is arrived at, expressing the charge fraction of monovalent to total ions as a function of the concentrations of the monovalent and divalent ions in the solution. To make it general, a case in which two diffuse double layers interact is considered.

The derivation given in the appendix rests on the following assumptions:

For a plate-shaped negatively charged colloid particle with the charge density σ on the plane surfaces, the distribution of mobile positive ions in the neighborhood of the surface

(the diffuse double layer) is given by the Poisson-Boltzmann differential equation in the one-dimensional form. Deviations from this one-dimensional form at edges and corners can be neglected, as the plates are very thin in comparison with their length and width.

The salt solution in equilibrium with the particles is made up of salts of the type M^+A^- and $M^{++}A^{--}$; for example, NaCl and $MgSO_4$.

The composition of the salt solution is taken at a point far from any surface. In practice it is the composition of a small volume of solution taken from a large volume of the whole suspension.

Interaction between the diffuse double layers of any two particles is considered under the assumption that the particles are orientated parallel to each other.

The charge fraction of monovalent to total ions in the double layer then reads

$$\frac{[Na]}{[Na + Mg]} = \frac{(Na)}{2\sqrt{Z} \cdot \sqrt{(Mg)}} \sinh^{-1} \frac{2\sqrt{Z} \cdot \sqrt{(Mg)}}{(Na) + (Mg) \cdot u_d} \quad (8)$$

where Z is related to the charge density of the surface by

$$Z = k \cdot \sigma^2$$

and thus has the dimensions of amount per unit volume, that is, concentration.

u_d is a function of the potential ψ_d in the midway plane between two surfaces, which can be written

$$-\frac{e\psi_d}{kT} = \cosh^{-1} \frac{u_d}{2} \quad (9)$$

where e is the charge of an electron, k is the Boltzmann constant, and T is the absolute temperature. From this it is seen that $\psi_d = 0$ when $u_d = 2$, which occurs when there is no interaction between the diffuse double layers.

An expression identical with (8) is obtained if in the derivation the influence of the negative ions in the diffuse double layer is neglected. Then, however, u_d is related to ψ_d by

$$-\frac{e\psi_d}{kT} = \ln u_d \quad (10)$$

At larger values of u_d , $\cosh^{-1} \frac{u_d}{2} = \ln u_d$, which shows that the influence of the negative ions may be small when the interaction is greater.

An expression similar to equation (4) (with $4Z$ instead of X) can be arranged from equation (8). The "constant" arrived at then is expressed by

$$K = \frac{\left[\sinh^{-1} \frac{2\sqrt{Z} \sqrt{(Mg)}}{(Na) + (Mg) \cdot u_d} \right]}{1 - \frac{(Na)}{2\sqrt{Z} \sqrt{(Mg)}} \sinh^{-1} \frac{2\sqrt{Z} \sqrt{(Mg)}}{(Na) + (Mg) \cdot u_d}} \quad (11)$$

Over a limited range of concentration, this "constant" need not vary much, and the greater is u_d the less does it vary; this is also true the larger (Na) and (Mg) .

To show the specific influence of the diffuse double layer on the distribution of monovalent and divalent ions in the swarm, K in equation (11) has been

calculated for varying values of $(Na) = (Mg)$. Z has been taken as 2, which corresponds approximately to the charge density for montmorillonite, and u_d is also taken as 2, that is, no interaction. The calculations are shown graphically in figure 1. K increases as the salt concentration in the solution decreases, which also means that the diffuse double layer extends farther out from the surface. It can be interpreted to mean that the activity coefficient for the monovalent ion in the swarm is lower at high dilution than in more concentrated solution.

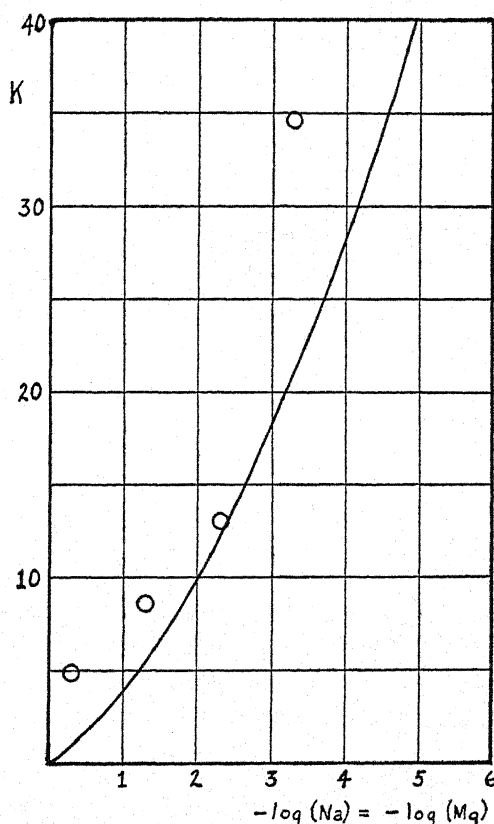


FIG. 1. CURVE REPRESENTING THEORETICAL VALUES OF K FROM EQUATION (11) WHEN $(Na) = (Mg)$, AND EXPERIMENTAL VALUES OF K (CIRCLES) CALCULATED FROM DATA BY MATTSON AND LARSSON (9) BY EQUATION (2).

This can be explained by considering the distribution of monovalent and divalent ions in the swarm at different points. Obviously, at a given potential distribution, the monovalent ions can extend farther out in the solution than the divalent. The space they occupy is greater than that for divalent ions, which are held more closely to the surface. At higher salt concentrations the extension of the diffuse double layer is decreased and the difference in "effective" volumes of the monovalent and divalent ions becomes less.

Mattson and Larsson (9) studied experimentally the influence of dilution of

the solution phase on the proportions of H_4N^+ and Ca^{++} in bentonite systems. From their values it is possible to calculate K from the equation

$$\frac{[H_4N^+]^2(Ca)4Z}{(H_4N^+)^2[Ca][H_4N + Ca]} = K \quad (12)$$

where the concentrations and amounts are given in equivalents and Z is equal to 2. As they kept $(H_4N^+) = (Ca^{++})$ for all dilutions, the constant K can be compared with the theoretical values according to equation (11) given in figure 1. The calculated values from the data of Mattson and Larsson have been plotted on the same graph; the agreement is, qualitatively, very good. The conditions under which Mattson and Larsson worked correspond very nearly to $u_d = 2$, that is, no interaction.

Equation (8) is of interest in another connection. If (Na') and (Mg') are the equivalent concentrations in the midway layer between two plates, they are related to the charge fraction of monovalent charges in the diffuse double layer by a very similar equation; namely,

$$\frac{[Na]}{[Na + Mg]} = \frac{(Na')}{2\sqrt{Z} \sqrt{(Mg')}} \sinh^{-1} \frac{2\sqrt{Z} \sqrt{(Mg')}}{(Na') + (Mg')} \quad (13)$$

an expression which can be of interest in connection with the activity of monovalent and divalent ions in a montmorillonite suspension or gel. But this is outside the scope of the present paper.

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APPENDIX

Charge fraction of monovalent ionic charges in a swarm at a negatively charged plane surface in equilibrium with a solution of monovalent and divalent ions

The symbols used are:

- ψ , the electric potential
- e , the charge of an electron
- k , the Boltzmann constant
- T , the absolute temperature
- ϵ , the dielectric constant of the medium
- x , the perpendicular distance from the surface
- ρ , the net charge density at a point x
- σ , the charge density of the surface
- n_1 , the number of monovalent ions per milliliter in the solution
- n_2 , the number of divalent ions per milliliter in the solution
- N , the Avagadro number.

It is assumed that the salts in the solution are of the type M^+A^- and $M^{++}A^{--}$, for instance, NaCl and $MgSO_4$.

The relation between the differential of the electric field and the net charge density is expressed by Poisson's equation, which in the one-dimensional form reads,

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi\rho}{\epsilon} \quad (1a)$$

The net charge density ρ can be expressed by the Boltzmann principle as a function of ψ , and in the case of monovalent and divalent ions it reads,

$$\rho = -2e \left(n_1 \sinh \frac{e\psi}{kT} + 2n_2 \sinh \frac{2e\psi}{kT} \right) \quad (2a)$$

and n_1 and n_2 are related to the equivalent concentrations of monovalent and divalent ions in the solution by

$$n_1 = c_1 \cdot N \cdot 10^{-3}$$

$$n_2 = \frac{c_2}{2} \cdot N \cdot 10^{-3}$$

Combining equations (1a) and (2a) and substituting c for n gives

$$\frac{d^2\psi}{dx^2} = \frac{8\pi e N \cdot 10^{-3}}{\epsilon} \left(c_1 \sinh \frac{e\psi}{kT} + c_2 \sinh \frac{2e\psi}{kT} \right) \quad (3a)$$

if $\frac{e\psi}{kT} = y$, then $\frac{d^2y}{dx^2} = \frac{e}{kT} \cdot \frac{d^2\psi}{dx^2}$ and

$$\frac{d^2y}{dx^2} = \frac{8\pi e^2 N \cdot 10^{-3}}{\epsilon kT} (c_1 \sinh y + c_2 \sinh 2y) \quad (4a)$$

With the boundary conditions $\frac{dy}{dx} = 0$ for $x = d$ when $y = y_d$ (as the distance between two surfaces is $2d$) $\frac{dy}{dx}$ can be solved and becomes

$$\frac{dy}{dx} = -\sqrt{\frac{16\pi e^2 N \cdot 10^{-3}}{\epsilon kT}} \sqrt{c_1(\cosh y - \cosh y_d) + c_2(\cosh^2 y - \cosh^2 y_d)} \quad (5a)$$

For convenience

$$\sqrt{\frac{16\pi e^2 N \cdot 10^{-3}}{\epsilon kT}} = \beta \quad (6a)$$

The charge density σ of the surface can be written

$$\sigma = - \int_0^d \rho \, dx = \frac{\epsilon}{4\pi} \int_0^d \frac{d^2\psi}{dx^2} \, dx = - \frac{\epsilon}{4\pi} \left(\frac{d\psi}{dx} \right)_{x=0} = - \frac{\epsilon k T}{4\pi e} \left(\frac{dy}{dx} \right)_{x=0}$$

$$\sigma = \frac{\beta \epsilon k T}{4\pi e} \sqrt{c_1(\cosh y_0 - \cosh y_d) + c_2(\cosh^2 y_0 - \cosh^2 y_d)} \quad (7a)$$

Writing
$$\frac{\sigma 4\pi e}{\beta \epsilon k T} = \sqrt{Z} \quad (8a)$$

and
$$\cosh y = \frac{u}{2} \quad (9a)$$

equation (7a) becomes

$$2\sqrt{Z} = \sqrt{2c_1(u_0 - u_d) + c_2(u_0^2 - u_d^2)} \quad (10a)$$

The quantity of monovalent ionic charges in the swarm per square centimeter of the surface is expressed by

$$\sigma_1 = -2c_1 N 10^{-3} e \int_0^d \sinh y \cdot dx \quad (11a)$$

which can be converted into an integral over y by use of equation (5a). Then

$$\sigma_1 = \frac{2c_1 N \cdot 10^{-3} e}{\beta} \int_{y_d}^{y_0} \frac{\sinh y \cdot dy}{\sqrt{c_1(\cosh y - \cosh y_d) + c_2(\cosh^2 y - \cosh^2 y_d)}} \quad (12a)$$

Using relation (9a) and remembering that its differential reads

$$\sinh y \cdot dy = \frac{du}{2}, \quad \text{we can write equation (12a)}$$

$$\sigma_1 = \frac{2c_1 N \cdot 10^{-3} e}{\beta} \int_{u_d}^{u_0} \frac{du}{\sqrt{2c_1(u - u_d) + c_2(u^2 - u_d^2)}} \quad (13a)$$

The integral

$$I = \int_{u_d}^{u_0} \frac{du}{\sqrt{2c_1(u - u_d) + c_2(u^2 - u_d^2)}}$$

is readily integrated and becomes

$$I = \frac{1}{\sqrt{c_2}} \ln \frac{\sqrt{2c_1(u_0 - u_d) + c_2(u_0^2 - u_d^2)} + \sqrt{c_2} \cdot u_0 + \frac{c_1}{\sqrt{c_2}}}{\sqrt{c_2} \cdot u_d + \frac{c_1}{\sqrt{c_2}}}$$

In this equation $\sqrt{2c_1(u_0 - u_d) + c_2(u_0^2 - u_d^2)}$ is readily identified as $2\sqrt{Z}$. Further, u_0 can be solved from equation (10a) and becomes

$$u_0 = \frac{\sqrt{(c_1 + c_2 \cdot u_d)^2 + 4c_2 Z} - c_1}{c_2}$$

Then the equation can be written

$$I = \frac{1}{\sqrt{c_2}} \ln \frac{2\sqrt{c_2 \cdot Z} + \sqrt{(c_1 + c_2 \cdot u_d)^2 + 4c_2 Z}}{c_1 + c_2 \cdot u_d}$$

which can be transformed into

$$I = \frac{1}{\sqrt{c_2}} \sinh^{-1} \frac{2\sqrt{c_2 Z}}{c_1 + c_2 \cdot u_d} \quad (14a)$$

and equation (13a) can be written

$$\sigma_1 = \frac{2c_1 N \cdot 10^{-3} \cdot e}{\beta \sqrt{c_2}} \sinh^{-1} \frac{2\sqrt{c_2 Z}}{c_1 + c_2 \cdot u_d}$$

As $\sigma = \beta \sqrt{Z} \cdot \frac{ekT}{4\pi e}$, the charge fraction $\frac{\sigma_1}{\sigma}$ becomes, after substitution of the value for β according to equation (6a),

$$\frac{\sigma_1}{\sigma} = \frac{c_1}{2\sqrt{c_2 \cdot Z}} \sinh^{-1} \frac{2\sqrt{c_2 Z}}{c_1 + c_2 \cdot u_d} \quad (15a)$$

A THERMOCHEMICAL APPROACH TO THE STUDY OF ION EXCHANGE¹

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Received for publication October 24, 1951

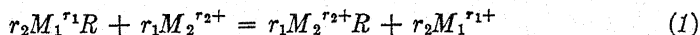
The energy changes that occur in the course of ion-exchange reactions are of considerable interest. Boyd *et al.* (1) have calculated standard free energies of formation of the salts of ion-exchange resins and metal cations. Marshall (8), from potentiometric measurements, has calculated "the difference between the differential heats of adsorption" of metal cations on clay membranes. Dawson *et al.* (2), also from potentiometric data, have calculated the heat of neutralization of H-peat with $\text{Ca}(\text{OH})_2$. So far as the author is aware, with the exception of some heats of neutralization of H-clays reported by Puri (10), no calorimetric data for ion-exchange reactions are available.

This paper reports some preliminary results of the calorimetric measurement of heats of neutralization of H-exchange resins and clays and of heats of reaction between exchange resin salts and electrolyte solutions. In addition, it attempts to relate measured heats of ion exchange to other thermodynamic functions.

THEORY

Heat of reaction, ΔH , is defined as the difference in heat content of products and reactants. For many reactions, ΔH can be measured experimentally by carrying out the reaction in a calorimeter and observing the temperature change. In principle, such calorimetric determination of ΔH is possible for ion-exchange reactions. The synthetic ion-exchange resins, because of their high exchange capacity, seem particularly well suited for such determinations. ΔH for an ion-exchange reaction, as well as free energy change and entropy change, is available also, in principle at least, from ion-exchange equilibrium data.

Consider the reaction:



Where R denotes the cation exchanger, $M_{1,2}$ are cations, and $r_{1,2}$ are valences of these cations. According to the mol fraction hypothesis, the equilibrium constant is given by:

$$k_{1-2} = \frac{C_2^{r_1}}{C_1^{r_2}} \cdot \frac{a_1^{r_2}}{a_2^{r_1}} \cdot (C_1 + C_2)^{r_2-r_1} \quad (2)$$

where C_1 and C_2 are the amounts in mols per liter of adsorbed ions and a_1 and a_2 are the molar activities of ions 1 and 2 in the solution phase, calculated from

¹ Paper No. 392 in the journal series; from the department of agronomy, North Carolina Agricultural Experiment Station.

the principle of ionic strength. From the statistical considerations of Krishnamoorthy and Overstreet (6):

$$k_{1-2} = \frac{C_2^{r_1}}{C_1^{r_2}} \cdot \frac{a_1^{r_2}}{a_2^{r_1}} \cdot (q_1 C_1 + q_2 C_2)^{r_2 - r_1} \quad (3)$$

The factor q_i is defined as $\frac{r_i + 1}{2}$ and the other symbols have the same meaning

as in equation (2). Data accumulated by various workers (1, 5, 6) show that equations (2) and (3) quite satisfactorily describe exchange equilibria for a variety of ion-exchange resins and clays.

Boyd *et al.* (1) and Kressman and Kitchener (5) have formally equated the negative logarithm of the equilibrium constant from equation (2) to the standard free energy change for the replacement of ion 2 by ion 1:

$$\Delta F^\circ = -RT \ln K_{1-2} \quad (4)$$

The latter authors have suggested that if the relation shown by equation (4) is accepted, it is possible, through the use of the Van't Hoff equation, to calculate ΔH° for an ion-exchange reaction from a knowledge of k , the equilibrium constant, at several temperatures.

$$\left(\frac{\partial \ln k}{\partial T} \right)_p = \frac{\Delta H^\circ}{RT^2} \quad (5)$$

The standard entropy change, ΔS° , for an ion-exchange reaction can be calculated from the relation:

$$\left(\frac{\partial \Delta F^\circ}{\partial T} \right) = -\Delta S^\circ \quad (6)$$

Thus from (4), (5), and (6) and a knowledge of the equilibrium constant, k , as a function of temperature, ΔH° , ΔF° , and ΔS° can be calculated for any ion-exchange reaction. Comparison of values for heat of reaction so obtained with those measured experimentally will provide a test for the thermodynamic consistency of the formulation of exchange equilibrium.

An entirely different approach to the problem of obtaining thermodynamic functions for ion-exchange reactions has been made by Marshall (8). He has identified the potential drop across a clay membrane separating solutions of two electrolytes with a common anion with the difference in mean activity of the two electrolytes and with the "difference between the differential heats of adsorption" of the two cations on the membrane. Marshall² recently agreed that his membrane theory should be developed in terms of free energy change rather than in terms of change in heat content.

Dawson and Danielson (2), from measured single ion activities, have calculated the intrinsic dissociation constant of H-peat and the equilibrium constant for the neutralization of H-peat with $\text{Ca}(\text{OH})_2$. From the equilibrium constant they have calculated the thermodynamic functions ΔF° , ΔH° , and ΔS° .

² Personal communication.

MATERIALS AND METHODS

A simple calorimeter was constructed. Two 1-pint Dewar flasks were immersed to within $\frac{1}{2}$ inch of their rims in a water bath at $30^{\circ} \pm 0.1^{\circ}\text{C}$. The mouths of the two flasks were fitted with cork stoppers with holes to accommodate a Beckmann thermometer, a stirrer, and a coil through which hot or cold water could be circulated. In addition, the flask in which reaction was to take place was fitted with a small funnel to facilitate addition of one of the reactants.

The synthetic exchange resins used in this investigation were Amberlites IR100, IR105, and IR120. The resins (40-mesh size) were treated with 5 per cent NaOH and carried through six cycles of leaching, first with 10 per cent HCl then with 10 per cent NaCl solutions. They were finally H-saturated by leaching with 10 per cent HCl, washed until free of chlorides, and air-dried. This is in agreement with standard procedures for the preparation of these materials.

The clay used was "Volclay" bentonite. H-clay was prepared by five successive treatments with symmetry concentration of HCl and was washed by centrifuging. In certain instances H-clay was prepared by leaching a suspension of Na-clay through a column of H-saturated IR120.

The titrable acidity of the various H-saturated exchange materials was determined by titration with NaOH to pH 8.2. Base-saturated materials were prepared by treating the H-form with an equivalent amount of the appropriate hydroxide.

The amount of exchange material used in the calorimetric measurements was 0.025 equivalent of the Amberlite and 0.005 equivalent of bentonite. This corresponds to 16.53 gm. IR100, 9.21 gm. IR105, 5.95 gm. IR120, and 7.27 gm. bentonite.

The following procedure was used to measure ΔH for an ion-exchange reaction: Into one of the two Dewar flasks comprising the calorimeter were placed a weighed amount of the ion-exchange material and a measured volume of water. Into the other flask was placed a measured volume of the solution with which the ion-exchange material was to react (MOH or MCl). Previously calibrated Beckmann thermometers were inserted into the flasks, and the temperatures of the contents were equalized by circulating water through the temperature control coils in the two flasks. Final adjustment of temperature could be satisfactorily made by circulating the same water through the coils of both flasks. When the temperatures of the two reactants were equal within 0.01°C ., the liquid reactant was quickly poured into the flask containing the exchange material in aqueous suspension.

After mixing, the temperature of the reaction flask was recorded as a function of time. All reactions studied were completed within 5 minutes. Extrapolation of the temperature rise due to heat of reaction and the temperature drop due to loss of heat to the surroundings yielded a value for ΔT corrected for heat loss. The temperature change, ΔT , multiplied by the heat capacity of the calorimeter and its contents and divided by the number of equivalents of products

formed, is reported as ΔH_{30° for the reaction in question. Each value of ΔH reported is the average of four measurements.

The heat capacity of the calorimeter was measured by means of the reaction:



The value of -13.3 Cal. per mol for the heat of formation of water from the ions was taken from Harned and Owen (3). It was not corrected for salt concentration. Heat capacities of liquid products and reactants were taken from the Handbook of Chemistry and Physics rather than from more exact sources. Heat capacities of resins and clay in suspension were arbitrarily assigned the value of 0.65 cal. per gram, the measured heat capacity of IR100. This seems justified, since the contribution of the clay or resin to the total heat capacity of the calorimeter and its contents was small, less than 5 per cent in all cases.

In measuring heats of neutralization, equivalent amounts of hydroxide were added to the various H-exchangers. For exchanges with salt solutions, sufficient

TABLE 1
Reproducibility of thermal data

REACTION	ΔT	HEAT CAPACITY	PRODUCTS	ΔH
	$^\circ\text{C.}$	<i>Cal.</i>	<i>mols</i>	<i>Cal./mol</i>
H-IR100 + KOH	+1.65	217	.025	-14.3
H-IR100 + KOH	+1.66	217	.025	-14.4
H-IR100 + KOH	+1.66	217	.025	-14.4
H-IR100 + KOH	+1.65	217	.025	-14.3
Na-IR100 + KCl	+0.07	217	.021	-0.7
Na-IR100 + KCl	+0.07	217	.021	-0.7
Na-IR100 + KCl	+0.08	217	.021	-0.8
Na-IR100 + KCl	+0.07	217	.021	-0.7

excess solution was added to afford virtually complete exchange. In most cases the solution was 1-2 *N* with respect to reacting electrolyte. At the completion of all determinations, an aliquot of supernatant liquid was analyzed to measure the extent to which the reaction had proceeded.

When concentrated electrolyte solutions were mixed with aqueous suspensions of the exchange materials, the observed temperature changes were corrected for the heats of dilution of the salt solutions used.

Admittedly, the procedure used to obtain the heats reported here was rather crude. The results obtained, however, appeared to be of sufficient value to warrant their publication.

Table 1 shows results typical of those obtained for neutralization reactions and for exchanges with salt solutions. Essentially the same results were obtained for four successive measurements.

The Beckmann thermometers were read to the nearest 0.01 $^\circ\text{C.}$ A cumulative readding error of 0.01 $^\circ\text{C.}$ would result in an error in ΔH of approximately 0.1 Cal. per mol for the Amberlites and 0.5 Cal. per mol for bentonite.

Equilibrium constants for exchange between various ion pairs were obtained at 10°, 30°, and 80°C. A weighed amount of M_1 -resin was equilibrated with a known amount of $M_2\text{Cl}$ in aqueous solution. At equilibrium the liquid phase was analyzed for M_1 and M_2 by standard methods. The amounts of adsorbed ions at equilibrium were calculated by difference. The activities of ions M_1 and M_2 in solution were obtained by multiplying the ion concentrations by appropriate powers of the electrolyte mean activity coefficients. Equilibrium constants were calculated with equation (3).

For the measurement of bi-ionic potential (the emf. across a membrane separating solutions of equal electrolyte mean activity, containing a common anion but different cations) membranes were prepared from the two resins and from "Volclay" bentonite as described by Wyllie and Patnode (12). Briefly, this involved molding a mixture of 60 per cent Na-exchanger and 40 per cent powdered polystyrene at 205°C. and 5,000 pounds per square inch. After molding, the membranes were attached to the ends of glass tubing by means of De Kottin-

TABLE 2
Heats of neutralization of H-exchange resins and H-clay
 ΔH_{25} Cal. per mol

BASE	IR100	IR105	IR120	BENTONITE	
				1*	2†
NaOH	-13.7	-13.5	-13.6	-5.8	-13.4
KOH	-14.4	-14.1	-14.2	-6.3	—
Ba(OH) ₂ ‡	-13.6	-13.3	-13.5	-5.8	—

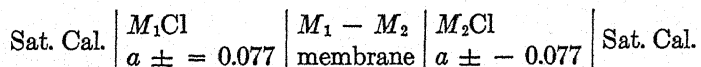
* H-saturated with HCl.

† Na-saturated and leached through a column of H-IR120.

‡ For the reaction $\text{HR} + \frac{1}{2}\text{Ba}(\text{OH})_2$.

ski cement. The membranes were tested as described by Marshall (8) and were found to yield emf. values in agreement with those predicted by the Nernst equation.

The membranes were soaked for several days in an equimolar solution of the chlorides of the two cations concerned. Finally, the membrane was incorporated in the cell:



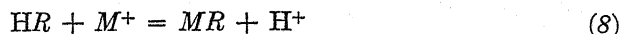
The two solutions $M_1\text{Cl}$ and $M_2\text{Cl}$ were changed repeatedly until the cell potential was constant.

RESULTS AND DISCUSSION

Heats of neutralization

Table 2 lists thermal effects observed to accompany the neutralization of H-exchange materials with various strong bases. ΔH is negative, that is, heat is evolved in all of the neutralization reactions.

Considering the over-all reaction between H-resin and MOH:



In the neutralization of a H-resin we have not one, but two reactions. The measured ΔH is the algebraic sum of the heats of reactions (8) and (9). In the case of the Amberlites, ΔH for the over-all reaction (table 1) is very nearly that for reaction (9), that is, the heat of formation of water from the ions. This leads to rather small values for ΔH_1 , the heat of exchange M^+ for H^+ .

ΔH 's for the neutralization of the clay are much smaller than those observed for the exchange resins. This may be interpreted in either of two ways: (a) Reactions (8) and (9) occur as written above, but ΔH for reaction (8) is large and

TABLE 3
 ΔH_{30} for the reaction $HR + M^+ = MR + H^+$

CATION-EXCHANGE MATERIAL	ΔH_{30} PER MOL			
	H-Na		H-K	
	1*	2†	1*	2†
	<i>Cal.</i>	<i>Cal.</i>	<i>Cal.</i>	<i>Cal.</i>
IR-100	-0.4	-0.3	-1.1	-1.0
IR-105	-0.2	-0.2	-0.8	-0.9
IR-120	-0.3	-0.3	-0.9	-0.9

* Calculated from measured heat of neutralization and heat of formation of H_2O from ions at 30° (-13.3 Cal. per mol).

† Measured for the reaction $HR + MCl$.

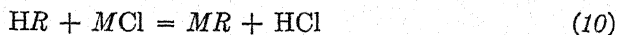
positive, that is, work is done in removing H^+ from the clay. (b) The reaction between a clay acid and MOH is not correctly shown by (8) and (9). This would be the case if the clay acid is actually a H-Al-clay (9). This latter possibility is supported somewhat by the measured heats of neutralization of H-clays prepared by leaching through columns of H-IR120. The heat of neutralization of H-bentonite so prepared is -13.4 Cal. per mol, as compared with a ΔH of -5.8 Cal. per mol when H-bentonite prepared with HCl is neutralized.

The figures reported in table 2 for the heat of neutralization of H-exchangers by $Ba(OH)_2$ are different in magnitude from the heat of neutralization of H-peat by $Ca(OH)_2$ reported by Dawson and Danielson (2).

Heats of ion exchange

If we consider that equations (8) and (9) correctly depict the reaction occurring when a H-resin is neutralized with a strong base, it follows that the difference between measured ΔH for the over-all reaction and ΔH for reaction (9) gives ΔH for reaction (8). In table 3, values for ΔH_{H-M} calculated from heats

of neutralization are compared with ΔH_{H-M} values measured by means of the reaction:



Agreement between the two sets of figures seems to be satisfactory.

Similarly, in considering the neutralization of a H-resin with various strong bases, it seems possible to identify the differences between the measured heats of neutralization with the differences between the heats of adsorption of the metal cations concerned.

Table 4 lists values for $\Delta H_{M_1-M_2}$ calculated from heats of neutralization values for $\Delta H_{M_1-M_2}$ measured for reactions of the sort:



The close correspondence between the two sets of ΔH 's seems to show that the thermal effects being measured are indeed changes in heat content occurring

TABLE 4
Heats of ion exchange

CATION EXCHANGE MATERIAL	ΔH_{25}° PER MOL						
	Li ⁺ -K ⁺	Na ⁺ -K ⁺		NH ₄ ⁺ -K ⁺	Ca ⁺⁺ -2K ⁺	Ca ⁺⁺ -Ba ⁺⁺	Ca ⁺⁺ -Mg ⁺⁺
		Measured	Calculated*				
IR-100	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.
IR-120	-1.4	-0.7	-0.7	-0.2	-2.7	-0.9	+0.2
	-1.2	-0.6	-0.6	-0.4	-2.5	-0.8	+0.2

* Calculated from data in table 2.

when one ion is substituted for another in the exchange complex. In this connection, ΔH for the reverse of a reaction such as (11) was found to be equal in magnitude but opposite in sign to that of the forward reaction.

Note in table 4 that ΔH for the reactions K-Li, K-Na, K-NH₄ decreases in the order given. This is the familiar series of adsorption affinities. Jenny (4) has related the affinity between cations and siliceous exchangers to the hydrated radii of the ions concerned, which are alleged to decrease in the order Li > Na > K = NH₄. More recently Boyd *et al.* (1), Kressman and Kitchener (5), and others have suggested that affinity may be related to the parameter, a° (the distance of closest approach), of Debye-Hückel theory. Following the suggestions of Kressman and Kitchener, changes in coulomb energy of interaction when one cation is replaced by another have been calculated from the relation e^2/Dd , where e is electronic charge, D is the dielectric constant of the medium (5), and d is the equilibrium distance of separation of the exchangeable ions from the exchange spots on the resin.

When a° for chloride salts (5) is substituted for d , the change in coulomb energy per mol is -0.8 Cal. for K-H exchange, -0.4 for Na-H exchange, -0.4 for K-Na

exchange, and -0.8 for K-Li exchange. Of course, the interaction between H^+ and exchange materials is not entirely electrostatic. When Jenny's values for the hydrated radii of ions are inserted for equilibrium distance of separation, the change in coulomb energy is -0.6 for K-Na exchange, -0.9 for K-Li exchange, and -0.3 for Na-Li exchange. On inserting Pallman's (7) values for hydrated radii we are led to changes in coulomb energy of -0.8 for K-Na exchange, -1.3 for K-Li exchange, -0.5 for Na-Li exchange. It is considered significant that measured heats of ion exchange and calculated changes in coulomb energy of interaction are of the same order of magnitude.

Note in table 4 that ΔH_{Ca-2K} is negative, that is, heat is evolved when K^+ replaces Ca on the resins IR100 and IR120. This is rather surprising, since ex-

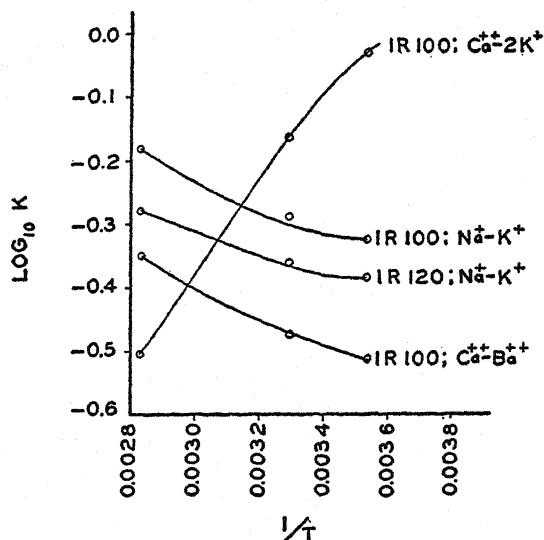


FIG. 1. EXCHANGE EQUILIBRIUM CONSTANTS AS FUNCTIONS OF TEMPERATURE

change studies show that, in general, Ca^{++} has a greater affinity for exchangers than does K^+ . This points to a large negative entropy change when monovalent ions replace divalent ions, at least in the reactions studied here. This may be related to changes in ion hydration on adsorption and desorption (5). It is also true that Ca ions can be arranged in more ways on the exchanger than can K ions.

Equilibrium constants and heat of reaction. Figure 1 shows $\log_{10} k$ as a function of $1/T$ for K-Na exchange with IR100 and IR120, for Ba-Ca exchange with IR100, and for Ca-2K exchange with IR100. To the four sets of data were fitted equations of the form:

$$\log_{10} k = \frac{A}{T} + B \log T + C \quad (12)$$

where A , B , and C are empirical constants, and T is absolute temperature. The values of the constants for the various exchange equilibria are listed in table 5.

The proper form of equation (12) was multiplied by the logarithmic modulus and differentiated with respect to T , assuming pressure to be constant. The resulting expression for $\left(\frac{\partial \ln k}{\partial T}\right)_d$ was substituted into equation (5). Values of ΔH_{30° calculated from the working equations are listed in column 5 of table 5. Calorimetrically measured heats of ion exchange are listed in column 6. Agreement between the derived and experimental values appears to be excellent.

The similarity of values for heats of ion exchange obtained experimentally and those calculated from equilibrium data suggests that equations (2) and (3) used to describe exchange equilibria are thermodynamically consistent. The possibility exists, however, that the thermodynamic equilibrium constants calculated with equations (2) and (3) are merely the ratios of the activity coefficients of the exchangeable ions.

TABLE 5

Empirical constants and derived values of ΔH°_{30} , ΔF°_{30} , and ΔS°_{30} for ion-exchange reactions

REACTION	A	B	C	ΔH_{30} PER MOL		ΔF°_{30} PER MOL	ΔS°_{30}
				Calculated	Measured		
				Cal.	Cal.	Cal.	e. u.
IR100:Na ⁺ -K ⁺	645	5.99	-17.270	+653	+700	+400	+0.84
IR120:Na ⁺ -K ⁺	283	3.05	-8.750	+545	+500	+498	+0.16
IR100:Ba ⁺⁺ -Ca ⁺⁺	133	2.63	-7.423	+979	+1000	+656	+1.06
IR100:Ca ⁺⁺ -2K ⁺	-301	-7.20	+18.691	-2686	-2700	+224	-9.64

* For exchange of Na⁺ for K⁺, with IR100:

$$\log K = \frac{645}{T} + 5.99 \log T - 17.270$$

$$\Delta H = \frac{d \ln k}{dT} \cdot RT^2 = -645 \cdot 2.303 \cdot R + 5.99 RT$$

$$\Delta F^\circ = -RT \ln k = -645 \cdot 2.303 \cdot R - 5.99 RT \log T + 17.270 \cdot 2.303 RT.$$

Considering the calculated values of ΔS° for the ion-exchange reactions, table 5 shows small entropy change for exchange between ions of the same valence. ΔS° for such exchanges is of the sign that would be predicted from a mechanistic consideration of the system, that is, an increase in entropy when an ion of low affinity replaces an ion of higher affinity.

ΔS° for the replacement of Ca⁺⁺ by K⁺ is large and negative. If we consider that there are more ways in which divalent ions can be arranged among the exchange sites than there are for univalent ions, the sign of the entropy change is as expected. If, as Krishnamoorthy and Overstreet suggest (6), exchange sites may be considered to be arranged in linear array, the possible number of different arrangements of divalent ions is twice that for univalent ions, and ΔS for the exchange of Ca⁺⁺ by K⁺ would be $-\ln 2 = 1.38$ e.u. The sign of ΔS° for the reaction is in accord with this prediction, but the magnitude is different.

Bi-ionic potentials. Potentials across membranes of IR100, IR120, and bentonite, separating solutions of different 1-1 electrolytes of equal mean activity

(0.077), are listed in table 6. The measured potentials are more negative in the order $\text{KCl-LiCl} > \text{KCl-NaCl} > \text{KCl-NH}_4\text{Cl}$. If the bi-ionic potential is identified with free energy change according to the equation,

$$\Delta F = -FE,$$

the values listed in table 6 under the heading " ΔF " are obtained. The columns in table 6 labeled " ΔF° " show for comparison the corresponding standard free energy changes calculated from equilibrium constants. Agreement seems to be excellent. Apparently Marshall's theory (8), modified to consider free energy change rather than heat of reaction, is substantially correct for the case of monovalent ions.

The measured potentials and calculated energy changes are of the same order of magnitude as those reported by Marshall (8) for bentonite and Putnam clay membranes. It should be pointed out, however, that in light of Sollner's (11) theory of bi-ionic potentials, the potential for a pair of univalent electrolytes

TABLE 6

Bi-ionic potentials and calculated ΔF_{30}° from the cell: Cal. | KCl | membrane | ACl | Cal.

MEMBRANE	LiCl-LiCl			KCl-NaCl			KCl-NH ₄ Cl		
	<i>E</i>	ΔF per mol	ΔF° per mol	<i>E</i>	ΔF per mol	ΔF° per mol	<i>E</i>	ΔF per mol	ΔF° per mol
	<i>mv.</i>	<i>Cal.</i>	<i>Cal.</i>	<i>mv.</i>	<i>Cal.</i>	<i>Cal.</i>	<i>mv.</i>	<i>Cal.</i>	<i>Cal.</i>
IR-100	33.8	-779	-734	20.1	-463	-400	1.0	-23	-17
IR-120	38.7	-892	-833	24.3	-561	-498	5.6	-129	-119
Bentonite	—*	—*	-1903	41.2	-950	-939	7.1	-163	-152

* Reproducible emf. values were not obtained for the KCl-LiCl.

would be a measure of the exchange constant only if the mobilities in the membrane of the two cations concerned were equal.

SUMMARY

Heats of neutralization of three H-exchange resins and one clay were measured calorimetrically. ΔH 's for the exchange of metal cations for hydrogen and for the interchange of metal cations were calculated from heats of neutralization. ΔH 's so obtained corresponded closely to those measured for the direct exchange of the cations concerned.

ΔH for the exchange of monovalent metal cations was of the same order of magnitude as was the expected change in coulomb energy of interaction. ΔH for the exchange of Ca^{++} by K^+ was negative, indicating that a large negative entropy change may occur when a monovalent cation replaces a divalent cation.

Data have been presented which show that calorimetrically measured heats of ion exchange are of similar magnitude to those calculated from equilibrium constants by means of the Van't Hoff equation. Free energy changes calculated from equilibrium constants agree with general observations concerning adsorption affinities. Entropy changes calculated for ion-exchange reactions are of the

sign expected from mechanistic consideration of the system. Marshall's theory of membrane potentials, developed in terms of free energy change rather than heat of reaction, is supported by experimental evidence.

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SOME THERMODYNAMIC PROPERTIES OF SOIL MOISTURE

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Received for publication August 6, 1951

Thermodynamic properties of soil moisture other than the free energy or moisture potential have received little consideration in past investigations. The present study involved evaluation of the specific heat content and specific entropy of soil moisture in addition to the specific free energy. From these properties, it is possible to draw more definite conclusions concerning the physical and energetic status of soil moisture as well as the mechanism of soil water retention.

The moisture potential or certain of the components of the moisture potential have been extensively studied since Buckingham (5) first applied the potential concept to soil water relations. Essential agreement exists as to the nature of the potential-moisture content relation, but methods for its evaluation have not been wholly satisfactory.

The vapor pressure method employed by Thomas (18, 19), Puri *et al.* (14), Edlefsen (6), Alexander and Haring (1), and others has contributed immensely to the understanding of the nature of the relation between moisture potential and moisture content. This method is still thermodynamically sound for such studies. Results obtained by such measurements withstand rigorous interpretation as the total moisture potential. Investigations by the vapor pressure method indicate that the moisture-potential-moisture-content function is essentially hyperbolic over a wide range of moisture contents.

Certain technical features make such measurements extremely difficult and lead to considerable uncertainty, especially in the range of high relative vapor pressure. Since this is the range of most practical significance, this objection is serious. A further limitation in the method is the so-called hysteresis effect in which soil samples that are initially dry fail to reach the moisture content attained by samples that were initially moist when placed in the same atmosphere.

The heat of wetting method has been employed by a number of investigators as a soil characteristic and in studies of the energetics of soil moisture. Anderson (2) and Bouyoucos (3) concluded that the heat of wetting is largely determined by the percentage of colloidal material present. Pate (13), in investigating the effect of the nature of replaceable cations upon the heat of wetting, concluded that the heat of wetting follows in general the lyotropic series.

Bouyoucos (4), Hoseh (9), and Puri and Hoon (15) have studied the effect of the moisture content on the heat of wetting. They concluded that increasing moisture content rapidly reduces the heat liberated. Puri and Hoon further concluded that the heat of wetting is appreciable up to about 0.90 relative vapor pressure, above which it becomes insignificant.

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Edlefsen and Anderson (7) have discussed a thermodynamic treatment for measurements of heat of wetting on soils. The interpretation proposed has been employed by Katz (10), by Fricke and Lüke (8), and by Stamm and Loughborough (16, 17) in such measurements for various organic colloidal systems. Such a treatment of heat of wetting data yields the thermodynamic property called the "specific heat content." Combination of the specific heat content values with specific free energy or moisture potential values yields a third thermodynamic property, the specific entropy.

The present study involved evaluation of the specific free energy by the static vapor pressure method and the specific heat content from heat of wetting measurements. From these two properties it was possible to compute the specific entropy, which permits conjecture as to the mechanism of soil moisture retention and the physical state of soil water.

EQUIPMENT AND METHODS

Vapor pressure determinations

The static vapor pressure method was used for evaluating the free-energy-moisture-content relations. Fourteen H_2SO_4 solutions producing a wide range of relative vapor pressures were prepared and placed in a series of vacuum desiccators. The desiccators were painted to exclude light and placed in a covered water bath maintained at constant temperature. As emphasized by Linford (11, 12), light falling upon the samples produces a heating effect which leads to serious errors in such determinations.

Three soils of the Yolo series with a wide textural range were used to present a diversity of moisture characteristics. Soil D-2 was a fine sandy loam with a moisture equivalent of about 13 per cent. Soil 53 was a clay with a moisture equivalent of about 26 per cent, and soil H-3 was a loam with a moisture equivalent of about 18 per cent. Two lots of each soil were prepared well in advance of the initial determinations. One lot was brought to a moisture content approximating the moisture equivalent, and the second lot was dried for several days in an oven at 85°C . These preparations were made to allow study of both the wetting and drying arms of the free-energy-moisture-content relations.

Determinations were made at three temperatures: 9.4°C , 19.9°C , and 29.9°C . Six replicate samples of about 2 to 3 gm. from both the moist and the dry lots of each soil were placed in each desiccator. The desiccators were sealed, evacuated, and allowed to remain in the bath for 76 to 95 days, a period considered sufficient for at least a close approach to the equilibrium values. At the end of this time, air was slowly admitted to the desiccators, the lids were removed, and the samples were quickly transferred to small weighing cans that had been previously dried and weighed. The samples were weighed, dried at 105°C ., reweighed, and the moisture contents determined. All weighings were made to 0.2 mgm., thus giving an accuracy of 0.01 per cent moisture content for each determination.

Each H_2SO_4 solution was titrated with a suitable standard NaOH solution immediately following each set of determinations, and the relative vapor pressure was determined graphically from data presented by Puri and Hoon (15).

Heat of wetting determinations

For the two finer textured soils employed in the vapor pressure analyses, calorimetric heat of wetting measurements were made by a technique similar to that of Puri and Hoon (15). The calorimeter consisted of a pint Dewar flask fixed into a cardboard cylinder and fitted with a Beckmann thermometer and stirrer. A pint Thermos bottle fitted with a stirrer and Beckmann thermometer served as the accessory vessel.

A measured quantity of water was added to the calorimeter, its temperature was recorded, and a second quantity of warmer water was then added from the accessory vessel. From the initial and final temperatures of the water in the calorimeter, the temperature of the water added, and the quantities of water involved, it was possible to evaluate the water equivalent of the calorimeter. The Beckmann thermometer settings were checked with a standard thermometer in a well-stirred water bath after each determination. All Beckmann readings were estimated to $0.001^{\circ}\text{C}.$, and the standard thermometer was estimated to $0.01^{\circ}\text{C}.$ This permitted measurements of temperature changes of about $0.002^{\circ}\text{C}.$ and simultaneously permitted evaluation of the temperature of the determination.

The specific heats of the soils used were determined by first adding a known quantity of soil to the calorimeter along with sufficient water to form a dilute suspension. The suspension was slowly stirred until thermal equilibrium was established. The temperature was then recorded, and a quantity of warmer water was added from the accessory vessel. From the initial and final temperatures of the suspension, the temperature of the water added, the water equivalent of the calorimeter, and the quantities of soil and water involved, the specific heat of the soil could be computed.

The heat of wetting measurements were made by first adding a known quantity of previously prepared soil to the calorimeter. The thermometer bulb was gently imbedded in the soil, and when thermal equilibrium was established, a small sample of the soil was removed for the moisture content determination. The temperatures of the soil and the water in the accessory vessel were recorded, and a quantity of the water was quickly added to the soil. The suspension was slowly stirred and the temperature periodically recorded until the final temperature was reached. All determinations were made at a temperature closely approximating that of the environment so that no temperature correction for the heat exchange between the calorimeter and surroundings was required.

From the water equivalent of the calorimeter and the specific heat of the soil, the temperatures involved, and the quantity of soil and water, it was possible to calculate the integral heat of wetting ΔQ or the heat exchange per gram of soil.

Heat of wetting measurements were made for the two soils at three temperatures corresponding to those of the vapor pressure determinations. The approximate mean temperatures of the determinations were 10.5 , 21.0 , and $27.5^{\circ}\text{C}.$, with most of the determinations falling within $0.75^{\circ}\text{C}.$ of the mean.

Determinations were made for moisture contents from oven-dryness to a value approaching the permanent wilting percentage for each of the soils used. Both

wetted and dried samples of each soil were used for comparison with similar treatments in the vapor pressure measurements. The wetted samples were those whose moisture content was attained by wetting with an atomizer; the respective moisture contents were attained for the dried samples by allowing water to evaporate from previously moistened soils. In each case, the samples were stored for a considerable period to allow moisture adjustments prior to the determinations.

TABLE 1

Results of vapor pressure determination at 9.4°C., showing moisture content and specific free energy for wetted and dried samples of three soils

SPECIFIC FREE ENERGY	MOISTURE CONTENT (DRY WEIGHT)					
	Soil D-2		Soil H-3		Soil 53	
	Wetted	Dried	Wetted	Dried	Wetted	Dried
10^{-3} ergs/gm.	per cent	per cent	per cent	per cent	per cent	per cent
-0.0027	6.4	7.2	8.4	10.5	12.2	15.6
-0.0039	6.1	7.0	7.8	9.7	11.2	13.9
-0.0105	5.6	6.8	7.4	9.5	11.0	14.2
-0.0171	5.5	6.3	7.0	8.6	10.3	12.4
-0.045	4.65	5.35	6.12	7.21	9.00	10.13
-0.133	3.84	4.59	5.08	6.04	7.02	8.39
-0.226	3.42	3.96	4.51	5.38	6.31	7.34
-0.480	2.42	2.97	3.27	4.08	4.78	5.59
-0.714	2.37	2.73	3.16	3.73	4.48	5.08
-0.946	2.20	2.52	2.89	3.45	4.07	4.61
-1.33	1.73	2.03	2.32	2.77	3.35	3.81
-1.81	1.57	1.75	2.06	2.36	2.99	3.30
-1.98	1.50	1.67	1.96	2.27	2.78	3.12
-3.34	1.12	1.23	1.39	1.62	1.98	2.24

EXPERIMENTAL

Vapor pressure determinations

Specific free-energy-moisture-content relations for the three soils employed at three temperatures are presented in tables 1, 2, and 3. The values of specific free energy were obtained by the following fundamental thermodynamic formula:

$$\Delta f = \frac{RT}{M} \ln \frac{P}{P_0} \quad (1)$$

where Δf is the specific free energy of the soil water, R is the universal gas constant, T is the absolute temperature, M is the molecular weight of water, and P and P_0 are the vapor pressure of the soil water and the vapor pressure of free water respectively. The moisture contents given represent the mean of the six replicates. For relative vapor pressures less than about 0.90, the individual moisture contents seldom varied more than 0.05 per cent from the mean. At higher relative vapor pressures the variations increased to as much as 0.2 per cent from

TABLE 2

Results of vapor pressure determinations at 19.9°C., showing moisture content and specific free energy for wetted and dried samples of three soils

SPECIFIC FREE ENERGY	MOISTURE CONTENT (DRY WEIGHT)					
	Soil D-2		Soil H-3		Soil 53	
	Wetted	Dried	Wetted	Dried	Wetted	Dried
10^{-9} ergs/gm	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
-0.0012	6.9	7.5	9.4	10.6	14.2	15.9
-0.0028	6.3	7.2	8.5	10.3	12.4	16.1
-0.0041	6.0	6.7	8.2	9.4	12.2	13.7
-0.0109	5.5	6.1	7.3	8.6	10.9	12.4
-0.0178	5.4	5.9	7.0	8.0	10.4	11.5
-0.0512	4.6	5.0	5.9	6.8	8.5	9.8
-0.144	3.83	4.29	5.10	5.84	7.16	8.12
-0.259	3.26	3.73	4.36	5.02	6.13	7.02
-0.527	2.51	2.85	3.45	4.01	4.73	5.39
-1.040	2.08	2.27	2.83	3.22	3.97	4.36
-1.458	1.85	1.95	2.51	2.80	3.41	3.72
-1.968	1.51	1.62	2.05	2.25	2.83	3.23
-2.264	1.32	1.45	1.78	2.06	2.47	2.82
-3.835	1.04	1.18	1.29	1.48	1.77	2.06

TABLE 3

Results of vapor pressure determination at 29.9°C., showing moisture content and specific free energy for wetted and dried samples of three soils

SPECIFIC FREE ENERGY	MOISTURE CONTENT (DRY WEIGHT)					
	Soil D-2		Soil H-3		Soil 53	
	Wetted	Dried	Wetted	Dried	Wetted	Dried
10^{-9} ergs/gm.	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
-0.0029	5.8	6.3	7.6	8.8	11.6	12.9
-0.0042	5.4	6.3	6.9	8.8	11.0	12.8
-0.0126	5.0	5.6	6.6	7.8	9.7	11.3
-0.0168	4.8	5.5	6.2	7.4	9.3	10.6
-0.0483	4.56	5.19	5.85	6.90	8.76	10.22
-0.137	4.05	4.53	5.29	6.15	7.59	8.60
-0.228	3.64	4.14	4.80	5.54	6.81	7.71
-0.514	2.83	3.25	3.72	4.29	5.30	5.91
-0.745	2.61	2.84	3.47	3.89	4.84	5.26
-1.15	2.21	2.34	2.86	3.18	4.11	4.43
-1.39	1.98	2.21	2.59	2.99	3.71	4.16
-2.07	1.56	1.67	1.99	2.30	2.89	3.16
-3.50	1.19	1.24	1.50	1.61	2.15	2.28

the mean, with even greater variability at relative vapor pressures in excess of 0.99.

Since it was desired to compare the specific free energy values with values

obtained from the heat of wetting measurements, it was necessary to determine specific free energy at specific moisture contents. The data were, therefore, plotted semilogarithmically, and an essentially straight line relation was found to exist over a major part of the curve, as reported by Alexander and Haring (1) for similar measurements on soil colloids.

Mathematical relations were derived for the exponential part of the curve to compute the specific free energy values desired. The expressions were of the form

$$\Delta f = a e^{-bm}, \quad (2)$$

where Δf is the specific free energy, m the fractional moisture content, a and b

TABLE 4

Integral heat-of-wetting-moisture-content relations for wetted and dried samples of soil 53 at three temperatures

10.5°C.				21°C.				27.5°C.			
Wetted		Dried		Wetted		Dried		Wetted		Dried	
Moisture content	Integral heat of wetting	Moisture content	Integral heat of wetting	Moisture content	Integral heat of wetting	Moisture content	Integral heat of wetting	Moisture content	Integral heat of wetting	Moisture content	Integral heat of wetting
<i>per cent</i>	<i>cal./gm.</i>	<i>per cent</i>	<i>cal./gm.</i>	<i>per cent</i>	<i>cal./gm.</i>	<i>per cent</i>	<i>cal./gm.</i>	<i>per cent</i>	<i>cal./gm.</i>	<i>per cent</i>	<i>cal./gm.</i>
0.93	-3.63	1.53	-3.03	0.80	-3.70	1.31	-3.13	0.56	-3.77	0.845	-3.65
1.80	-2.49	2.49	-2.05	1.63	-2.60	2.18	-2.10	1.47	-2.45	0.925	-3.38
2.34	-1.96	3.52	-1.13	2.30	-1.96	2.80	-1.60	2.11	-1.83	1.24	-2.88
3.10	-1.29	3.65	-1.27	2.89	-1.33	3.31	-1.21	2.60	-1.40	2.45	-1.66
4.23	-0.715	4.11	-0.941	4.16	-0.701	4.27	-0.854	3.89	-0.665	3.09	-1.16
5.52	-0.398	5.70	-0.433	5.47	-0.413	5.46	-0.467	5.24	-0.369	4.05	-0.730
7.82	-0.149	6.72	-0.253	7.79	-0.139	6.54	-0.321	7.53	-0.118	4.29	-0.692
10.01	-0.068	7.36	-0.178	10.07	-0.046	7.72	-0.191	9.83	-0.0299	5.42	-0.480
		8.03	-0.123							5.46	-0.391
		8.29	-0.152							7.02	-0.218
		9.36	-0.087							7.59	-0.196

are constants, and e is the base of natural logarithms. These expressions satisfactorily fit the data for the specific free energy range 0.02×10^9 to 3.5×10^9 ergs per gram. In some of the comparisons which follow, the expressions have been extrapolated somewhat beyond these limits and the values so obtained are somewhat questionable. It was felt, however, that as a first approximation such errors would not be serious in the present investigation.

Heat of wetting determinations

Integral heats of wetting for the two soils employed at three temperatures are presented in tables 4 and 5. The values of ΔQ , the integral heat of wetting, are negative in sign to concur with the accepted thermodynamic convention that heat liberated is negative. Each of the values represents the mean value for four to eight replicate determinations. The individual moisture content values seldom varied by more than 0.05 per cent from the mean. The integral heats varied from

3 to 5 per cent from the mean at the lower moisture contents and as much as 25 to 30 per cent at the highest moisture contents. These relatively high percentage errors were, however, not serious because of the small quantities of heat involved.

For a thermodynamic interpretation of the heat of wetting measurements, it is not the integral heat of wetting ΔQ which is of most interest. This quantity represents the heat exchange per gram of soil, initially at an arbitrary moisture content m , upon its immersion in an excess of water. The heat exchange upon the addition of a gram of water to a large mass of soil already at moisture content m is of greater thermodynamic significance. This quantity, which is referred to as

TABLE 5

Integral heat-of-wetting-moisture-content relations for wetted and dried samples of soil H-3 at three temperatures

10.5°C.				21°C.				27.5°C.			
Wetted		Dried		Wetted		Dried		Wetted		Dried	
Moisture content	Integral heat of wetting	Moisture content	Integral heat of wetting	Moisture content	Integral heat of wetting	Moisture content	Integral heat of wetting	Moisture content	Integral heat of wetting	Moisture content	Integral heat of wetting
per cent	cal./gm.	per cent	cal./gm.	per cent	cal./gm.	per cent	cal./gm.	per cent	cal./gm.	per cent	cal./gm.
1.61	-1.32	0.73	-2.73	0.25	-3.00	0.55	-2.62	0.29	-2.78	0.39	-2.76
1.82	-1.16	1.40	-1.72	0.48	-2.70	1.72	-1.33	0.78	-2.04	1.12	-1.82
1.93	-1.08	3.18	-0.592	0.92	-2.04	1.82	-1.21	1.30	-1.42	1.25	-1.62
2.47	-0.701	4.77	-0.242	1.36	-1.52	1.95	-1.14	1.81	-1.00	1.33	-1.57
2.64	-0.641	5.87	-0.112	1.82	-1.11	2.61	-0.801	2.34	-0.726	1.55	-1.32
2.74	-0.648	6.09	-0.125	2.34	-0.752	3.19	-0.573	2.64	-0.523	2.60	-0.722
3.52	-0.315	7.75	-0.052	2.80	-0.549	4.47	-0.248	3.34	-0.301	3.10	-0.525
3.73	-0.381	7.89	-0.041	3.71	-0.325	5.19	-0.159	3.60	-0.321	4.36	-0.242
5.31	-0.150	8.30	-0.021	4.11	-0.259	5.84	-0.107	4.00	-0.195	5.80	-0.097
8.15	-0.043			5.23	-0.129	6.08	-0.077	5.07	-0.119	7.04	-0.047
				6.36	-0.064	6.97	-0.066	6.07	-0.038		
				7.46	-0.036			6.51	-0.046		
				8.74	-0.030			7.39	-0.020		

the differential heat of wetting $\left(\frac{\partial q}{\partial m}\right)_T$, represents the change in specific heat content Δh during the process.

The method for obtaining the differential heat of wetting values from the integral heat of wetting determinations is described by Edlefsen and Anderson (7). It consists simply of determining the heat exchange Δq in bringing a sample of soil from zero moisture content up to the moisture content m in question. These values of Δq are then plotted against the fractional moisture content m , and the slope of the curve obtained is the value of the differential heat of wetting $\left(\frac{\partial q}{\partial m}\right)_T$ or the specific heat content Δh .

The values of Δq are obtained at successive moisture contents by computing the difference between the integral heat of wetting ΔQ_0 at zero moisture content

and the integral heat of wetting ΔQ at the moisture content in question. Obviously, the curve representing the difference $\Delta Q_0 - \Delta Q$ plotted against the moisture content as described is merely the complement of the relation between the integral heat of wetting ΔQ and the moisture content. Therefore, the slopes or first differentials of the two relations are numerically equal but opposite in sign at any arbitrary moisture content. Thus, the differential heat of wetting $\left(\frac{\partial q}{\partial m}\right)_T$ can be determined merely by changing the sign of the slope or first differential of the integral heat of wetting relations.

This method was employed in the present investigation for determining the differential heat of wetting. The data from tables 4 and 5 were plotted semi-logarithmically, and, as for the specific free energy functions, a straight line relation was found to exist over a wide range of moisture contents. Mathematical expressions were derived and differentiated. Negative values of the first differential obtained represent the differential heat of wetting or specific heat content.

DISCUSSION

Specific free energy relations

Values for the specific free energy at a series of moisture contents were computed for the three soils at the three temperatures. The relations differed only in the location of the curves. Figure 1 illustrates the nature of the relation and the magnitudes involved for soil 53 at 9.4°C. Data for both wetted and dried samples are depicted with experimental and computed points. The so-called hysteresis effect, or the failure of wetted and dried samples to attain equivalent moisture contents, was evident in each case for all moisture contents employed and was of comparable magnitude for each soil at the three temperatures.

The relations are typical of previously published vapor pressure data. The values of specific free energy were negative for all moisture contents studied and increased numerically in an exponential manner with reducing moisture content. The relatively small reduction in specific free energy at the higher moisture contents illustrates one of the serious limitations in the vapor pressure method for studies of the energy relations of soil moisture. This relatively small change in specific free energy with changes in moisture content produces considerable uncertainty as to the exact nature of the relations in this range. For the present investigation, however, it is felt that the relations are sufficiently clear-cut for the comparisons and computations to be made.

The variation of the specific free energy with temperature was not conclusive from the vapor pressure study. For the wetted samples, it appears that the specific free energy increases numerically with increases in temperature. The change appears to be, to a first approximation, directly proportional to the ratio of the absolute temperatures. For the dried samples, a similar relation exists for the determinations at 9.4 and 29.9°C. The values at 19.9°C., however, were numerically smaller than the values at 9.4°C. The nature of the data and the

small apparent changes in specific free energy with temperature preclude an exact statement concerning this variation.

Specific heat content relations

Specific heat content or differential heat of wetting values for the two soils employed were computed for the same moisture content values as those used in the specific free energy calculations. All the relations were identical in form and varied only in location of the curves. Figure 2 illustrates the nature of the relations and the magnitudes involved for soil 53 at 10.5°C. As in the specific free energy relations, the values for the wetted and dried samples again displayed

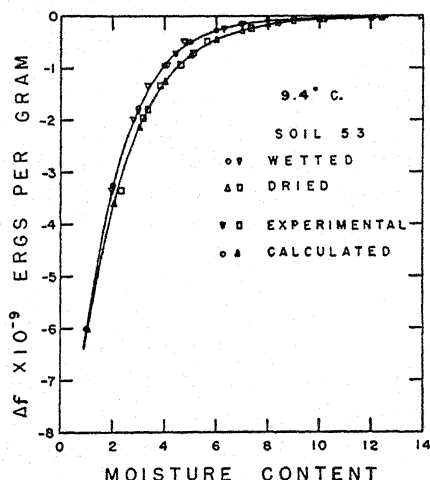


FIG. 1

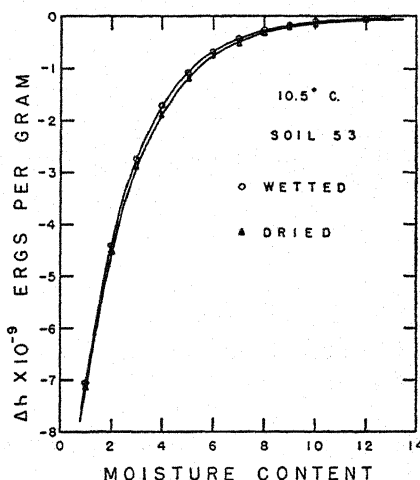


FIG. 2

FIG. 1. SPECIFIC-FREE-ENERGY-MOISTURE-CONTENT RELATIONS FOR WETTED AND DRIED SAMPLES OF SOIL 53 AT 9.4°C.

FIG. 2. SPECIFIC-FREE-ENERGY-MOISTURE-CONTENT RELATIONS FOR WETTED AND DRIED SAMPLES OF SOIL 53 AT 10.5°C.

the hysteresis effect. Although the magnitude of the effect was not so large as in the specific free energy values, its appearance in the specific heat content values is further evidence of the reality of the effect.

The occurrence of the hysteresis effect in vapor pressure studies has been attributed to failure to allow sufficient time for establishment of equilibrium. Although about 3 months were allowed in this study, the vapor pressure measurements are subject to the same criticism. The heat of wetting measurements do not depend on this time factor. Such measurements are governed by the state of the soil system at the time of its immersion. It is believed, therefore, that the appearance of the hysteresis effect in the specific heat content values is more concrete evidence of the reality of the effect than are the vapor pressure data. It should be pointed out, however, that neither of the measurements constitutes absolute proof of the existence of the effect, nor does it suggest explicitly the

mechanism involved if the effect is real. Possibly the effect appears, not because of its inherence in the nature of the soil moisture system, but rather because of physical alterations in the samples incurred during their preparation for the measurements.

As in the specific free energy relations, all values of the specific heat content were found to be negative for the soil moisture contents studied. The values increased numerically in an exponential manner with decreasing moisture content. The measurements were limited to the relatively dry soil moisture range because of the small quantities of heat exchanged at higher moisture contents. Possibly at higher moisture contents the values may assume a positive magnitude.

The specific heat content values show considerable variation with temperature. In contrast to the specific free energy values, the specific heat content was found to decrease numerically with increases in temperature.

A comparison of the magnitudes in figures 1 and 2 shows that at all moisture contents studied, the specific free energy is exceeded in numerical magnitude by the specific heat content. From these two relations it is possible to calculate a third thermodynamic property, the specific entropy, by means of Gibbs' equation:

$$\Delta s = \frac{\Delta h - \Delta f}{T}, \quad (3)$$

where Δs is the specific entropy, T the absolute temperature, and Δh and Δf the specific heat content and specific free energy respectively. This property was computed for both wetted and dried samples of the two soils at three temperatures. Although the temperatures of the vapor pressure and heat of wetting measurements were not equal in all cases, the differences were not so great as to cause serious errors in the specific entropy computations.

Since the specific heat content values in all cases exceeded the specific free energy values in numerical magnitude, the specific entropy assumed a negative sign. All of the specific entropy relations were similar in nature, with a tendency to decrease in numerical magnitude with increasing temperature. Figure 3 illustrates the specific entropy relation for dried samples of soil 53 at the lower temperature along with the specific free energy and specific heat content relations from which it was obtained. The hysteresis effect also appeared in the specific entropy values, but the indirect methods used in obtaining these values may produce errors as large as or larger than the differences obtained between the values for the wetted and dried samples. In addition, the values of specific entropy obtained at the lowest moisture contents displayed a decreasing numerical magnitude, and in some cases even a positive value was obtained at the arbitrary zero moisture content. These values are extremely questionable because of the extrapolation required in obtaining the values from which they were computed.

The specific entropy values obtained are essentially the same as those reported by Stamm and Loughborough (16, 17) for wood and for cotton. Fricke and Lüke (8) in a similar study of agar found the specific entropy to be reduced but constant over a wide range of moisture contents. Their findings indicate the similarity in the moisture-energy relations between soils and certain organic materials.

The negative entropy values obtained are highly significant with regard to the mechanism of soil water retention and the physical state of soil water. The entropy is a thermodynamic measure of the randomness of a system, negative values indicating a reduction in randomness. The negative values obtained indicate a reduction in randomness of soil water, at least in the range studied. This reduced randomness might be caused either by orientation or by association of the water molecules. Changes in association or orientation may be caused by a variety of mechanisms in the soil moisture system. It is well established that several forces may be coexistent in soil moisture retention, and the predominance of certain forces in certain moisture regions results in the continuous nature of the specific-free-energy-moisture-content relation. This same interaction of forces results in the continuous-entropy-moisture-content relation, and the predom-

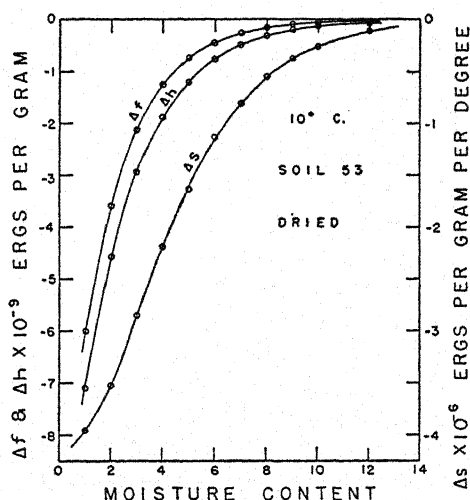


FIG. 3. SPECIFIC FREE ENERGY, SPECIFIC HEAT CONTENT, AND SPECIFIC ENTROPY AS A FUNCTION OF MOISTURE CONTENT FOR DRIED SAMPLES OF SOIL 53 AT ABOUT 10°C.

inant forces in the moisture content range studied are those producing orientation or association with accompanying negative specific entropy values.

Three types of forces acting in soil water retention in the range of moisture contents studied probably produce negative specific entropy values. First, the presence of the water within the electric force field should produce orientation of the water molecules. Second, positive hydrostatic pressure within the water films resulting from the attraction of superimposed molecular layers should produce association or orientation. Third, hydration of ions or precipitated salts should produce a reduced randomness.

The electrostatic forces of the electric force field attract the water molecules and retain them in a more or less rigid lattice structure, thus reducing their freedom of movement. This effect is manifest for some distance from the soil particle surface. It is reduced rapidly with increasing distance from the soil particle surface because of the rapid reduction in field strength. The attraction of the water

molecules beyond the molecular layer immediately adjacent to the soil particle results in positive hydrostatic pressures within the underlying layers. This positive pressure reduces the freedom of movement of the water molecules. These same effects would be present in hydrated ions or hydrated salt molecules. The water of hydration would possess less freedom of movement than would free water, and the ionic forces present would reduce the randomness of adjacent water molecules in addition to those held rigidly as water of hydration. Negative pressures or tensions due to surface tension forces would result in increased randomness with positive entropy values. A combination of these forces results in the negative entropy values obtained in the present investigations.

It thus appears that the dominant forces in water retention in soils for all moisture contents, at least up to the permanent wilting percentage, are the electric field forces and, to a lesser extent, the salts present in the soil solution. The surface tension forces apparently remain of secondary importance at least up to this moisture content. This predominance helps to explain the rapid change in slope of the specific-free-energy-moisture-content relation as the moisture content approaches the permanent wilting percentage.

SUMMARY AND CONCLUSIONS

The present investigation was undertaken to obtain a more complete understanding of the energetics of soil moisture and to establish more clearly the nature of the forces involved in soil moisture retention. The methods employed were chosen primarily because of their thermodynamic rigidity; other deficiencies in the methods were considered of secondary importance.

Each of the three thermodynamic properties investigated (the specific free energy, the specific heat content, and the specific entropy) was found to be reduced at all moisture contents studied. The specific free energy and specific heat content each exhibited the characteristic hysteresis effect, thus supporting its reality in the soil moisture system. The methods employed in obtaining the specific entropy, however, prevent any conclusive statement concerning the hysteresis effect in this property.

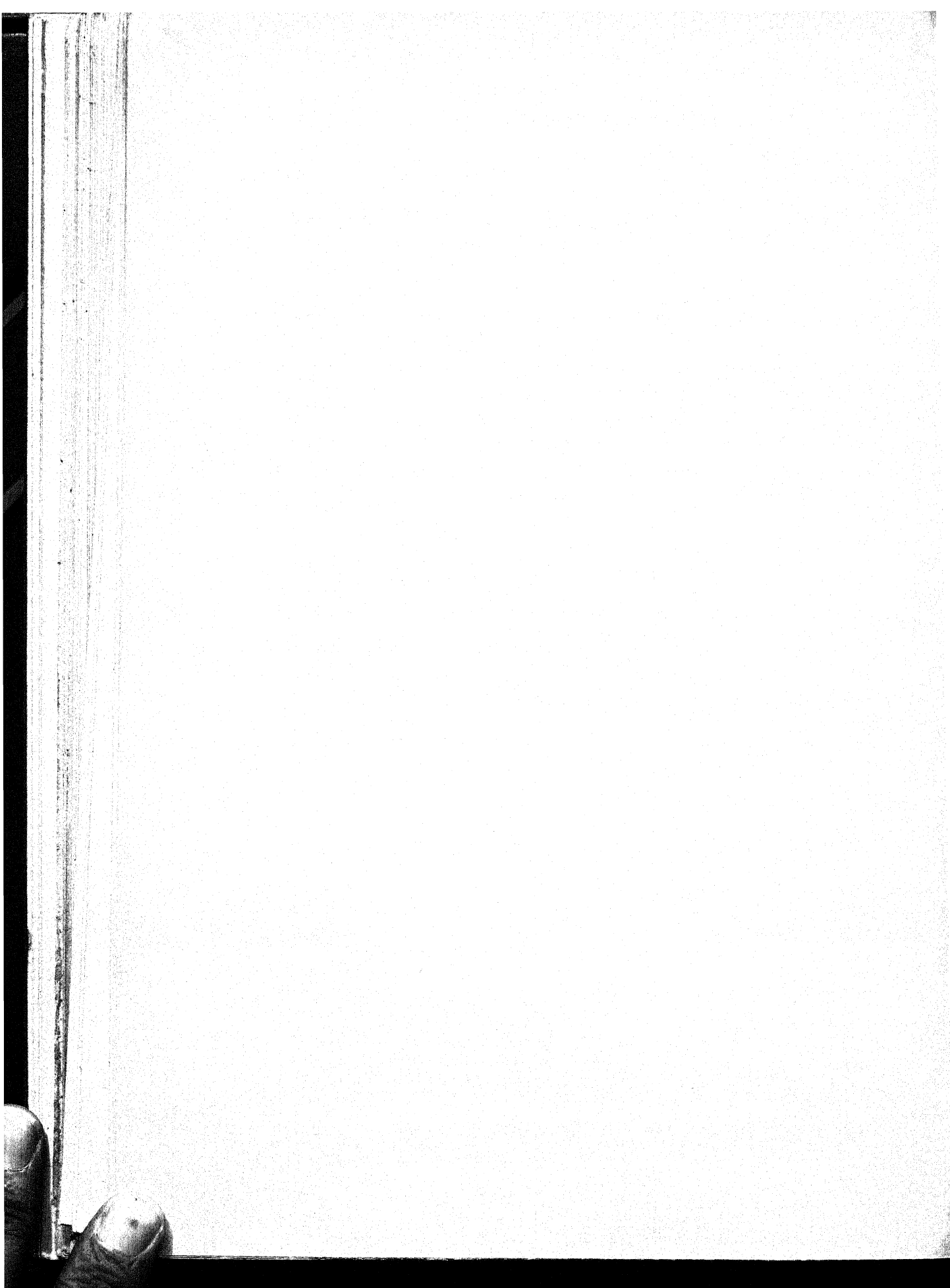
The specific free energy, the specific heat content, and the specific entropy were found to be affected somewhat by temperature for the temperature range studied. The specific free energy was found to increase numerically with increasing temperature, but the change was neither large nor consistent. The specific heat content and specific entropy were found to decrease numerically with increasing temperature.

The negative specific entropy values show that the randomness of the soil moisture is reduced over the range of moisture contents studied. This reduced randomness indicates that the major contributor to soil moisture retention for moisture contents, at least up to the permanent wilting percentage, is the electric force fields surrounding the soil particles.

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ROLE OF THE FLUORIDE ION IN RELEASE OF PHOSPHATE ADSORBED BY ALUMINUM AND IRON HYDROXIDES

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Received for publication October 18, 1951

The role of the fluoride ion in the release of adsorbed phosphate has received considerable attention from soil chemists (1, 3, 6, 11). Swenson, Cole, and Sieling (11) showed that the fluoride ion, when its concentration was in excess of six moles of fluoride to one mole of aluminum, prevented the precipitation of phosphate by aluminum ion, whereas the corresponding effect when aluminum was replaced with ferric ion was very slight. They concluded that the efficiency of the fluoride ion in releasing colloid-bound phosphate depended on its ability to form stable complexes with iron and aluminum.

The results reported here, in which x-ray analysis was used to identify the products of the reaction between the hydroxide gels of aluminum or ferric iron and ammonium fluoride, support the conclusions of Swenson *et al.*

ADSORPTION OF PHOSPHATE BY ALUMINUM AND IRON HYDROXIDES AND ITS RELEASE BY THE FLUORIDE ION

Aluminum and ferric hydroxide gels were prepared by adding NH_4OH in slight excess to aqueous solutions of the nitrate salts of the metals. The supernatant liquids were removed by centrifugation, and the gels washed with water to which a trace of NH_4OH had been added. Each batch of prepared gel was washed into a large flask, and water was added to give a specific volume. The amount of $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$ present was determined by evaporating to dryness and igniting aliquots of the suspensions. One-hundred-milliliter aliquots of H_3PO_4 with concentrations ranging from 0.89 to 114 ppm. P, all adjusted to pH 7 with NH_4OH , were mixed with portions of the gels for 5 minutes and the supernatant liquids centrifuged off. The amount of gel used in each case represented 150 to 250 mgm. of ignited oxide. The phosphate adsorbed was calculated from the decrease in its concentration in solution due to contact with the gels. The method described by Kurtz (5) was used in determining phosphate concentration in solution.

The curves in figure 1, which are representative of the results showing the relation between the equilibrium concentration in solution (5-minute contact) and the amount adsorbed by the gels, could all be represented reasonably well by the adsorption isotherm $y = ax^n$, where y is milligrams of P adsorbed per gram of metal oxide and x is the equilibrium concentration in solution expressed as parts per million P. The experimental results with the $\text{Fe}(\text{OH})_3$ gel precipitated from a cold solution (curve C, fig. 1) did not follow the calculated curve very well but

¹ Scientific Contribution No. 212 of the Division of Chemistry, Science Service, Ottawa, Canada. The petrographic examinations were made by L. M. Patry of this laboratory.

this was thought to be caused by rather serious peptization of the gels, especially at the higher concentrations of phosphate. The differences in the isotherms for each hydroxide were apparently caused by the different treatments of the gels, as indicated in figure 1.

The gels, after treatment with the phosphate solutions, were extracted with 100-ml. aliquots of neutral N NH_4F , and the phosphate in the supernatant liquids was determined. The significant difference in the efficiency of neutral N

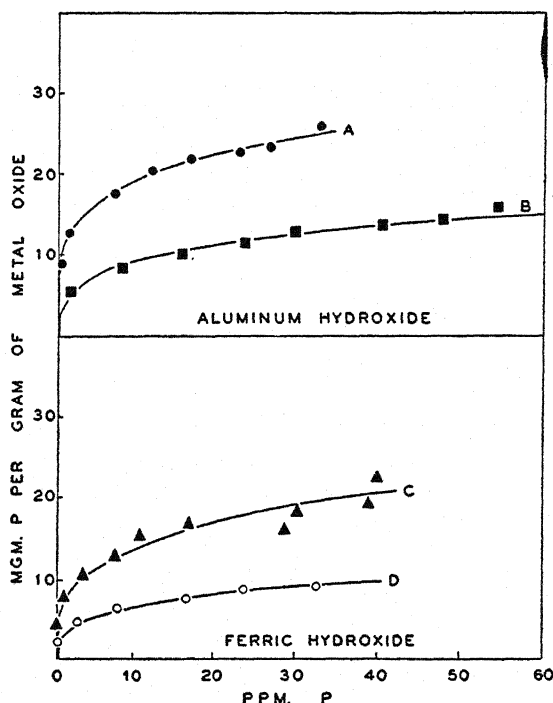


FIG. 1. RELATION BETWEEN EQUILIBRIUM CONCENTRATION IN SOLUTION (PPM. P) AND PHOSPHATE ADSORBED BY GELS (MGM. P/GM. METAL OXIDE)

A: hydroxide precipitated from a hot solution, $y = 12.30 x^{0.208}$. B: hydroxide precipitated from a hot solution and aged for 6 weeks, $y = 4.40 x^{0.308}$. C: hydroxide precipitated from a cold solution, $y = 7.78 x^{0.267}$. D: hydroxide precipitated from a hot solution, $y = 2.84 x^{0.350}$. (y = mgm. P adsorbed per gm. metal oxide, x = ppm. P in solution after 5 minutes).

NH_4F as an extractant of phosphate adsorbed by $\text{Al}(\text{OH})_3$ compared with its efficiency when the phosphate was adsorbed by $\text{Fe}(\text{OH})_3$ is apparent from comparison of table 1 with table 2. Table 1 shows that roughly 90 per cent of the phosphate adsorbed by $\text{Al}(\text{OH})_3$ was released with one 24-hour extraction by NH_4F and more than 60 per cent was extracted in 5 minutes. On the other hand, when $\text{Fe}(\text{OH})_3$ was the adsorbent (table 2), less than 9 per cent of the phosphate was released in 5 minutes by the NH_4F when the adsorbent was freshly precipitated from a hot solution, and none at all when the adsorbent was precipitated from a cold solution even though the time of extraction was 24 hours.

The relative efficiency of neutral NH_4F as an extractant of phosphate adsorbed by $\text{Al}(\text{OH})_3$ compared with its efficiency when the phosphate was adsorbed by $\text{Fe}(\text{OH})_3$ corresponds to the stabilities of the complexes formed by the two metals with fluoride. Aluminum-fluoride complexes are more stable than are iron-fluoride

TABLE 1
Phosphate adsorbed by $\text{Al}(\text{OH})_3$ and released by NH_4F

$\text{Al}(\text{OH})_3$ FRESHLY PRECIPITATED FROM A HOT SOLUTION		$\text{Al}(\text{OH})_3$ PRECIPITATED FROM A HOT SOLUTION AND AGED 6 WEEKS		
P adsorbed per gram metal oxide	P released by NH_4F , 24-hour contact	P adsorbed per gram metal oxide	P released by NH_4F	
			5-minute contact	24-hour contact
<i>mgm</i>	<i>per cent</i>	<i>mgm.</i>	<i>per cent</i>	<i>per cent</i>
8.7	89.3	8.2	62.9	
15.7	90.6	9.8		92.9
20.3	92.0	11.1	69.8	
22.9	93.1	13.4		90.1
26.1	96.4	13.5	66.7	
		14.7		97.7
		16.5	72.1	
		15.9		91.5
		16.6	66.7	
		16.6		96.1
		17.1	70.8	

TABLE 2
Phosphate adsorbed by $\text{Fe}(\text{OH})_3$ and released by NH_4F

$\text{Fe}(\text{OH})_3$ FRESHLY PRECIPITATED FROM A COLD SOLUTION		$\text{Fe}(\text{OH})_3$ FRESHLY PRECIPITATED FROM A HOT SOLUTION	
P adsorbed per gram metal oxide	P released by NH_4F , 24-hour contact	P adsorbed per gram metal oxide	P released by NH_4F , 5-minute contact
<i>mgm.</i>	<i>per cent</i>	<i>mgm.</i>	<i>per cent</i>
3.9	0	0.6	8.7
7.7	0	2.7	2.5
10.9	0	4.2	3.5
12.8	0	6.6	5.7
15.3	0	7.0	6.5
16.8	0	8.7	8.9
15.9	0	8.8	6.9
19.0	0		
19.3	0		
23.0	0		

complexes (4). Experiments were therefore made, using x-ray analysis, to determine the effect of neutral NH_4F on the hydroxides of aluminum and ferric iron.

X-RAY DIFFRACTION STUDIES OF THE REACTION BETWEEN NH_4F AND THE GELS OF ALUMINUM AND IRON HYDROXIDES

Since, as shown subsequently, the mole ratio of fluoride to total iron or aluminum in the reaction mixtures was far in excess of 6, the coordination number of

the two metals, the most likely products of the reactions appeared to be $(\text{NH}_4)_3\text{AlF}_6$ and $(\text{NH}_4)_3\text{FeF}_6$. Ammonium fluoaluminate is insoluble in water containing NH_4F or NH_4OH (8), and the x-ray diffraction angles of the pure salt are available. Furthermore, this complex aluminum-fluoride salt can be prepared by treatment of $\text{Al}(\text{OH})_3$ with a solution of NH_4F (2, 8). It was only necessary, therefore, to show to what extent NH_4F reacted with $\text{Al}(\text{OH})_3$ under conditions similar to those under which it was used as an extractant of adsorbed phosphate. The solid $(\text{NH}_4)_3\text{FeF}_6$ has apparently not received so much attention as has its aluminum counterpart. The compound has been isolated, however, and its crystal structure studied (7, 10), but the x-ray diffraction pattern is apparently not available in the literature.

Pure $(\text{NH}_4)_3\text{AlF}_6$ and $(\text{NH}_4)_3\text{FeF}_6$ were prepared by dissolving the nitrate salts of aluminum or ferric iron in alcohol and then adding solid NH_4F to give a mole ratio of fluoride to aluminum or iron in excess of 6, sufficient alcohol being used so that NH_4NO_3 did not precipitate. The precipitates were washed with alcohol

TABLE 3
Analysis of the fluoride complexes of aluminum and iron

$(\text{NH}_4)_3\text{AlF}_6$			$(\text{NH}_4)_3\text{FeF}_6$		
	Found	Theoretical		Found	Theoretical
	<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
NH_4	27.3	27.7	NH_4	24.3	24.1
Al.....	13.7	13.9	Fe.....	24.9	25.0
F.....	58.4	58.4	F.....	49.8	50.9
Total.....	99.4	100.0	Total.....	99.0	100.0

until free from soluble ammonium salts and dried under vacuum. The analyses of the compounds, shown in table 3, agree satisfactorily with the theoretical values. Petrographic examination showed that both compounds were platey isotropic crystals. The samples were ground to pass a 350-mesh screen for x-ray analysis. Similarity between the two compounds is indicated in table 4, which shows the d spacings and relative intensities of the diffraction lines (the strongest line being given the value 100 for each compound) obtained with a Phillips x-ray spectrometer, and the (hkl) values calculated from $a_0 = 8.9$ for the aluminum complex (9) and $a_0 = 9.1$ for the iron complex (10). Data for the aluminum complex taken from A.S.T.M. index card No. 3-0122 are included in table 4 for comparison. Since the crystals were flat, care was taken to minimize orientation in preparing the spectrometer specimens. A Norelco Cu tube with Ni filter was used for these and all subsequent aluminum compounds; a Norelco Fe tube with Mn filter was used for the iron compounds.

Samples of $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$ gels, representing approximately 200 mgm. of ignited oxide, were treated with 100-ml. aliquots of neutral N NH_4F . The residues were washed with water containing a trace of NH_4OH , dried under vacuum, and

ground to pass a 350-mesh screen for x-ray analysis. The results are presented in figures 2, 3, and 4.

Figure 2 A and D shows the x-ray spectrometer patterns of $\text{Al}(\text{OH})_3$ precipitated from a hot solution and of $(\text{NH}_4)_3\text{AlF}_6$. B, which represents $\text{Al}(\text{OH})_3$ (A) treated for 5 minutes with NH_4F , shows that, in this short time, reaction had taken place to such an extent that $(\text{NH}_4)_3\text{AlF}_6$ predominated in the reaction mixture. When the reaction time was 18 hours, the x-ray pattern (C) was almost identical with that for pure $(\text{NH}_4)_3\text{AlF}_6$ (D).

TABLE 4

Data from diffraction patterns of the fluoride complexes of aluminum and iron

A.S.T.M. INDEX CARD NO. 3-0122		$(\text{NH}_4)_3\text{AlF}_6$			$(\text{NH}_4)_3\text{FeF}_6$		
		Found			Found		
dA	I/I	dA	I/I	(hkl)	dA	I/I	(hkl)
5.20	100	5.16	100	111	5.28	100	111
4.47	60	4.47	63	200	4.57	61	200
3.14	60	3.16	57	220	3.23	45	220
—	—	—	—	—	2.75	6	311
2.57	30	2.59	27	222	2.63	8	222
2.22	100	2.24	42	400	2.28	29	400
2.03	4	2.05	6	331	2.07	6	331
1.99	4	2.00	6	420	2.04	11	420
1.82	12	1.82	10	422	1.86	16	422
1.71	25	1.72	18	333 [511]	1.75	14	333 [511]
1.58	16	1.58	8	440	1.61	9	440
1.50	12	1.51	6	531	1.54	9	531
1.48	4	1.49	3	600 [442]	1.52	6	600 [442]
1.41	14	1.42	8	620	1.44	5	620
1.36	4	1.37	2	533			
1.29	6	1.29	2	444			
1.25	8	1.25	3	711			
1.19	12	1.19	5	642			
1.16	6	—	—	—			

Figure 3 A shows that aging $\text{Al}(\text{OH})_3$ for 7 hours under hot water produced a gel with strong, sharp diffraction lines. Figure 3 B, C, D, and E illustrate the fact that NH_4F reacted slowly with aged $\text{Al}(\text{OH})_3$. The lines in B, which resulted from a reaction time of 5 minutes, are somewhat shorter than those for the pure $\text{Al}(\text{OH})_3$ but none of the lines characteristic of $(\text{NH}_4)_3\text{AlF}_6$ (E) is evident. When the reaction time was 18 hours (C) the lines characteristic of both $\text{Al}(\text{OH})_3$ and the aluminum-fluoride complex were clearly represented; the pattern for the 43-hour reaction time (D) shows the lines characteristic of the pure $(\text{NH}_4)_3\text{AlF}_6$ predominating.

The fact that neutral NH_4F had no measurable effect on $\text{Fe}(\text{OH})_3$ is illustrated in figure 4. There is virtually no difference between A, pure $\text{Fe}(\text{OH})_3$, and B,

$\text{Fe}(\text{OH})_3$ treated for 18 hours with NH_4F . Furthermore, there is no indication that the lines in C, pure $(\text{NH}_4)_3\text{FeF}_6$, appear in B.

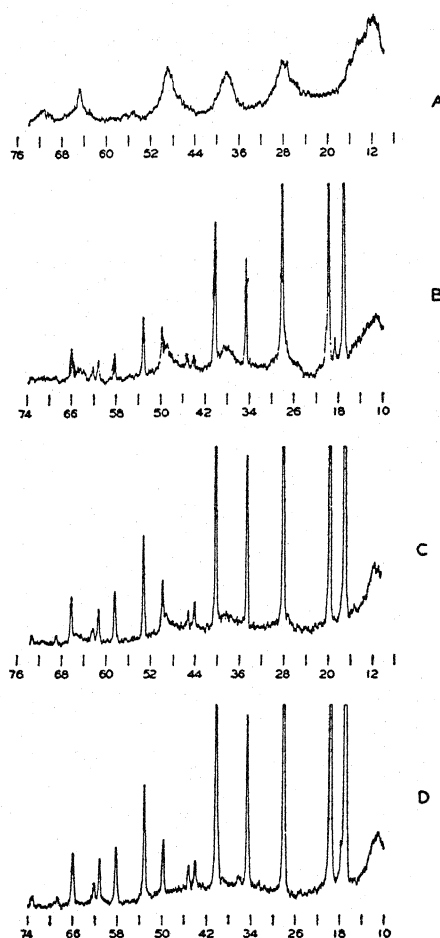


FIG. 2

FIG. 2. X-RAY SPECTROMETER PATTERNS SHOWING THE EFFECT OF NEUTRAL AMMONIUM FLUORIDE ON ALUMINUM HYDROXIDE FRESHLY PRECIPITATED FROM A HOT SOLUTION
A: aluminum hydroxide. B: aluminum hydroxide treated for 5 minutes with fluoride. C: aluminum hydroxide treated for 18 hours with fluoride. D: ammonium fluoaluminate.

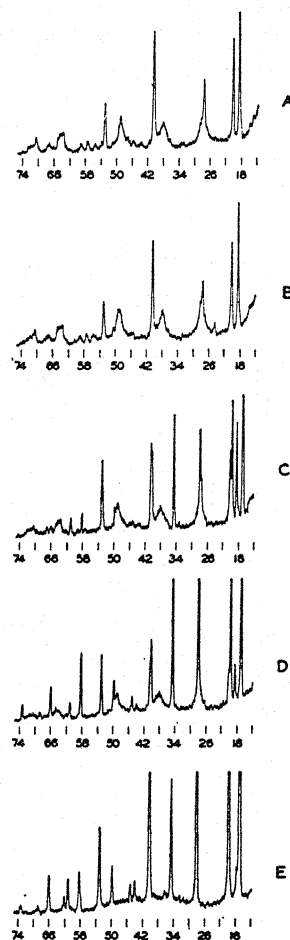


FIG. 3

FIG. 3. X-RAY SPECTROMETER PATTERNS SHOWING THE EFFECT OF NEUTRAL AMMONIUM FLUORIDE ON ALUMINUM HYDROXIDE AGED FOR 7 HOURS UNDER BOILING WATER
A: aluminum hydroxide. B: aluminum hydroxide treated for 5 minutes with fluoride. C: aluminum hydroxide treated for 18 hours with fluoride. D: aluminum hydroxide treated for 43 hours with fluoride. E: ammonium fluoaluminate.

As was expected from the foregoing experiments, $\text{Fe}(\text{OH})_3$ could be precipitated in presence of an excess of NH_4F , although a yellow gel resulted instead of the usual reddish brown one, but addition of NH_4OH to an acid solution of

$\text{Al}(\text{NO}_3)_3$ in presence of an excess of NH_4F always resulted in a precipitate of $(\text{NH}_4)_3\text{AlF}_6$. An x-ray pattern of a residue obtained by taking an acid solution of $\text{Fe}(\text{NO}_3)_3$ and NH_4F to dryness showed the lines characteristic of $(\text{NH}_4)_3\text{FeF}_6$, which indicated that the trivalent fluoferrate ion was present in the acid solution.

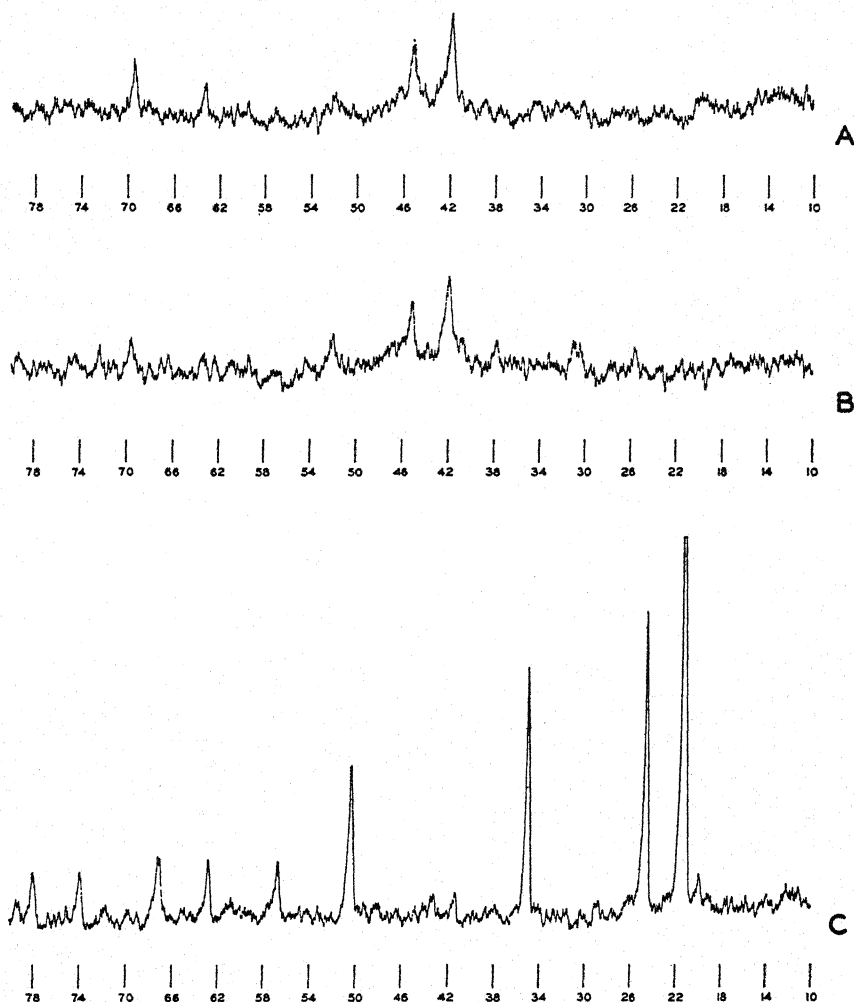


FIG. 4. X-RAY SPECTROMETER PATTERNS SHOWING THE EFFECT OF NEUTRAL AMMONIUM FLUORIDE ON FERRIC HYDROXIDE

A: ferric hydroxide. B: ferric hydroxide treated for 18 hours with fluoride. C: ammonium fluoferrate.

SUMMARY AND CONCLUSIONS

Neutral NH_4F reacted with $\text{Al}(\text{OH})_3$ gels to form $(\text{NH}_4)_3\text{AlF}_6$, and phosphate adsorbed by these gels was more or less completely released by the action of the fluoride. On the other hand, $\text{Fe}(\text{OH})_3$ gels were apparently not attacked by the

fluoride, and the phosphate adsorbed was not released to any extent. The efficiency of neutral NH_4F as an extractant of phosphate adsorbed by $\text{Al}(\text{OH})_3$ is explained by the stability of the trivalent fluoaluminate complex ion in neutral and alkaline solutions, the phosphate adsorbed being made soluble by the direct action of the fluoride ion on the gel with the formation of a nonadsorbent aluminum-fluoride complex. Apparently the trivalent fluoferrate ion, formed in acid solutions, is destroyed in neutral and alkaline solutions with the formation of $\text{Fe}(\text{OH})_3$.

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ADSORPTION OF MONONUCLEOTIDES, NUCLEIC ACIDS, AND NUCLEOPROTEINS BY CLAYS

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Received for publication November 23, 1951

Nucleic acid materials introduced into soil by incorporation of plant and animal residues or synthesized by soil microorganisms have been presumed to contain a major portion of the soil organic phosphorus (2, 21). Dephosphorylation of these materials in soils might provide crops with appreciable amounts of phosphorus during the growing season (7, 15, 19). When nucleic acid materials were intimately mixed with the clay minerals that occur in soils, however, enzymatic dephosphorylation was retarded (2). Determination of the nature of adsorption of nucleic acid materials by clays therefore seemed desirable.

Adsorption of nucleic acid materials by soils and clays has been observed (2, 4, 16). Soils with high clay content adsorbed the largest amounts of these materials (16). Bower (2) found that adsorption of guanine nucleotide, nucleic acid, and nucleoprotein from yeast by kaolinite or bentonite occurred over a wide pH range. Adsorption increased with decreased pH, and bentonite adsorbed larger amounts of these materials than did kaolinite. Bower suggested that adsorption of nucleic acid materials by negatively charged clays was probably due in part to the presence of basic groups which gave the materials a positive charge under acid conditions.

The present investigation was undertaken to determine the factors affecting the adsorption of mononucleotides, nucleic acids, and nucleoproteins by kaolinite, illite, and bentonite.

MATERIALS AND METHODS

The preparation of the H-kaolinite, H-illite, and H-bentonite fractions has been described in a previous paper (12). The range in diameter of the coarse clay fractions was 5 to 0.5μ , of the fine kaolinite and illite fractions below 0.5μ , and of the fine bentonite fraction 0.5 to 0.15μ .

Yeast ribonucleic acid² was purified by standard methods (9, 20). The purified product contained 15.8 per cent nitrogen, 9.1 per cent total phosphorus, and 0.04 per cent inorganic phosphorus. There was little difference between the original and the purified samples, and the composition of both samples was similar to the theoretical composition of ribonucleic acid (17). Neither the original sample nor the purified material contained detectable amounts of metallic cations. The average size of a molecule of the purified ribonucleic acid was estimated, by titration, to be equivalent to 5 or 6 mononucleotides.

¹ Journal Paper No. J-2023 of the Iowa Agricultural Experiment Station, Ames, project 1070; work supported by the Industry Phosphate Research Committee. Taken in part from a thesis submitted by the senior author in partial fulfillment of the requirements for the degree of doctor of philosophy in soil bacteriology, 1950.

² Obtained from Fisher, Eimer, and Amend Co., New York.

Desoxyribonucleic acid³ contained 8.1 per cent total phosphorus and 0.57 per cent inorganic phosphorus. Most of the inorganic phosphorus was removed by dissolving the original material in NH_4OH and reprecipitating it in acidified 75 per cent $\text{C}_2\text{H}_5\text{OH}$. The mononucleotide preparations, guanylic and cytidylic acids from yeast⁴ and 3-adenylic acid from yeast,⁵ contained negligible amounts of inorganic phosphorus and were almost free of metallic cations. The nucleoprotein used was protamine nucleate.⁶

A mixture of inositol phosphates containing about 70 per cent hexaphosphate and 25 per cent pentaphosphates and quatrphosphates (18) was prepared.⁷

In the general procedure employed, the desired quantity of clay suspension was mixed on an end-over-end shaker with other appropriate materials in a 15-ml. pyrex tube. The mixture was centrifuged at 2,000 r.p.m., and the total phosphorus content of the supernatant liquid was determined (6). The centrifuged material was brought into suspension, and the pH value of the suspension was determined with a Beckman pH meter. Toluene, and occasionally thymol, were used as bacteriostatic agents to minimize growth of microorganisms. These substances affected neither the pH values of the suspensions nor the adsorption properties of the materials. Experiments were conducted at $25^\circ \pm 2^\circ\text{C}$. unless otherwise stated.

RESULTS

Primarily, it was of interest to determine the general nature of adsorption of nucleic acid materials by clays. Accordingly, the effects of several factors on adsorption were studied. An understanding of the chemical and physical reactions that take place was also desirable. Thus, an attempt was made to determine the chemical groups involved and the ways in which they take part in the reactions between nucleic acid materials and clays.

General nature of adsorption

Rate of adsorption of ribonucleic acid by coarse clay fractions. It was necessary to determine when the initial reactions between nucleic acid materials and clays reached equilibrium before comparisons could be made of the effects of different factors on equilibrium adsorption. Preliminary experiments indicated that the initial reaction between ribonucleic acid and bentonite approached equilibrium within 24 hours and reached equilibrium within 72 hours. Subsequently, a more extensive study was made of the effect of time, ribonucleic acid concentration, and NaOH concentration on the rate at which ribonucleic acid was adsorbed by clays.

Suspensions of coarse H-bentonite, H-illite, and H-kaolinite to which had

³ Obtained from Krishell Laboratories, Portland, Oregon.

⁴ Purchased from Nutritional Biochemicals Corporation, Cleveland, Ohio.

⁵ Furnished by the bacteriology department, Iowa State College.

⁶ Obtained from Nutritional Biochemicals Corporation.

⁷ Prepared and furnished by R. H. Jackman, department of Agronomy, Iowa State College.

been added different amounts of NaOH were mixed with ribonucleic acid in varying concentrations, and adsorption was measured after different periods. Adsorption after 48 hours was assumed to be 100 per cent, and the percentage of maximum adsorption that had occurred within each period up to 48 hours was calculated. The results obtained are shown in table 1.

TABLE 1

Adsorption of ribonucleic acid phosphorus by coarse clay fractions during different periods and in presence of different amounts of NaOH

CLAY SUSPENSION	NaOH ADDED PER GM. OF CLAY	TOTAL RIBO- NUCLEIC ACID P PER ML. OF SUSPENSION	ADSORPTION OF RIBONUCLEIC ACID P				
			P adsorbed per gm. of clay in 48 hours	Adsorption in indicated period as a percentage of P adsorbed in 48 hours			
				1 hour	3 hours	6 hours	24 hours
	<i>mc.</i>	<i>mgms.</i>	<i>mgms.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
H-bentonite 0.1 per cent	0	0.015	10.90	79.8	—	81.6	85.4
		0.030	18.70	89.4	—	92.0	97.7
		0.045	26.00	82.7	—	89.5	94.2
	0.30	0.015	7.70	76.6	—	79.2	85.7
		0.030	16.50	79.4	—	89.1	96.4
		0.045	24.40	80.7	—	84.4	90.6
	0.60	0.015	5.50	60.0	—	85.5	96.4
		0.030	12.80	78.9	—	85.2	93.0
		0.045	19.70	76.7	—	90.0	94.4
	0.90	0.015	2.80	46.5	—	71.5	78.5
		0.030	9.60	67.6	—	76.0	89.5
		0.045	16.20	71.6	—	84.0	91.4
H-illite 0.5 per cent	0	0.010	1.56	87.3	89.8	—	96.2
		0.020	2.87	91.3	94.1	—	99.2
		0.030	4.50	83.6	90.1	—	98.2
	0.20	0.010	0.21	66.6	66.6	—	71.5
		0.020	0.90	62.3	73.4	—	93.4
		0.030	1.60	81.2	85.1	—	92.5
H-kaolinite 1.0 per cent	0	0.010	0.66	80.0	83.4	—	100.0
		0.020	1.04	87.5	91.3	—	94.2
		0.030	1.42	78.2	83.1	—	97.1
	0.04	0.010	0.15	60.0	80.0	—	86.7
		0.020	0.58	69.0	86.0	—	88.0
		0.030	0.92	91.3	95.6	—	98.0

There was little increase in adsorption of ribonucleic acid after 24 hours. Almost invariably, more than 60 per cent of maximum adsorption had taken place within 1 hour. Probably, rapid chemical reaction first occurred, followed by a rearrangement of the ribonucleic acid molecules to allow maximum adsorption possible. There were no significant differences in the rates of adsorption of ribonucleic acid phosphorus by the three clays although adsorption approached a maximum more rapidly with kaolinite than with illite or bentonite. The most pronounced differences in adsorption of ribonucleic acid by the clays occurred

within the first hour. The rate of reaction increased as the concentration of ribonucleic acid was increased and the concentration of NaOH was decreased. The reaction between clay and NaOH may have influenced the rate at which ribonucleic acid molecules were absorbed by the clay.

The effect of temperature on the rate of the reaction between ribonucleic acid and bentonite was also determined. Adsorption after 1 hour was slightly greater at 45°C. than at 7°C. After 96 hours, there was no appreciable difference in adsorption between temperatures. It appears, therefore, that an increase in temperature increased the rate of the reaction but did not change appreciably equilibrium adsorption.

All of the factors investigated influenced the rate at which ribonucleic acid was adsorbed by the clays. Nevertheless, the reaction approached equilibrium within 24 hours. Thus equilibrium adsorption under varying conditions could be measured after 24 hours, and differences obtained would not be confounded with differences in the rate of reaction.

Equilibrium adsorption of mononucleotides, nucleic acids, and protamine nucleate by coarse clay fractions. The rate of reaction of ribonucleic acid with clays having been established, experiments were conducted to determine the effect of pH and organic phosphorus concentration on equilibrium adsorption of nucleic acid materials by coarse clay fractions. A preliminary experiment indicated that adsorption of ribonucleic acid phosphorus per gram of bentonite decreased with increased clay concentration although total adsorption increased. Subsequently, suspensions of the coarse clay fractions to which NaOH had been added were mixed with solutions of ribonucleic acid for 72 hours. The results are illustrated in figure 1.

Adsorption increased with decreased pH or increased concentration of ribonucleic acid. With a constant amount of adsorption, the concentration of ribonucleic acid phosphorus in solution increased as the pH values of the suspensions increased. At equivalent pH values, total ribonucleic acid concentrations, and equilibrium ribonucleic acid concentrations, adsorption of phosphorus per gram of clay by bentonite was about 6 times greater than by illite and 20 times greater than by kaolinite.

Additional experiments showed that the adsorption behavior of ribonucleic acid in the presence of kaolinite, illite, or bentonite when $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$ was employed was similar in nature to its behavior when NaOH was employed. There were, however, certain differences. These differences are indicated by the experimental results illustrated in figure 2. These results were obtained by measuring adsorption of ribonucleic acid phosphorus by bentonite either saturated to different degrees with sodium, calcium, or magnesium, or saturated to different degrees with sodium and suspended in *N* solutions of NaCl, KCl, CaCl_2 , and MgCl_2 . The concentration of bentonite was 0.1 per cent in the former suspensions and 0.05 per cent in the latter. All of the suspensions contained 0.015 mgm. of ribonucleic acid phosphorus per milliliter and were mixed for 24 hours before analyses were made for adsorption.

At equal pH values, adsorption in presence of calcium or magnesium was greater than in presence of sodium or potassium. Adsorption in presence of

NaCl did not differ significantly from that in presence of KCl, and that in presence of calcium was not significantly greater than that in presence of magnesium. Adsorption did not decrease as much with increasing pH in the presence of the divalent cations as it did in the presence of the monovalent cations.

Adsorption of guanylic acid, cytidylic acid, and 3-adenylic acid by Na-H-bentonite, and of cytidylic acid by Na-H-kaolinite, was determined. The adsorption behavior of these compounds was different in degree but similar in nature to adsorption of ribonucleic acid. At equivalent pH values, clay concentrations, and organic phosphorus concentrations, mononucleotides were adsorbed to about one third the degree of ribonucleic acid. The relative degree of adsorption

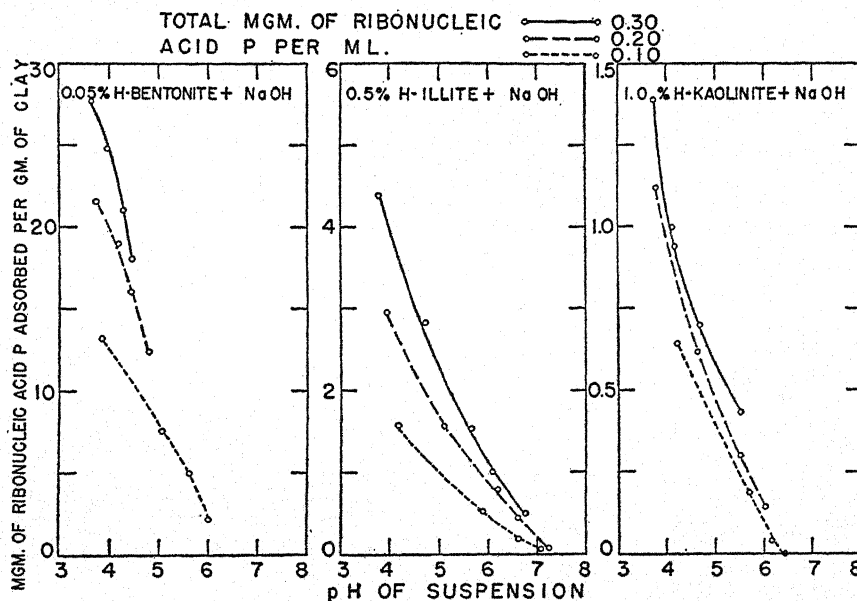


FIG. 1. ADSORPTION OF RIBONUCLEIC ACID PHOSPHORUS BY H-CLAYS ADJUSTED TO DIFFERENT pH VALUES WITH NaOH

was 3-adenylic acid > cytidylic acid > guanylic acid, but the differences between mononucleotides were small. At equivalent pH values, total cytidylic acid concentrations, and equilibrium cytidylic acid concentrations, adsorption of cytidylic acid phosphorus per gram of bentonite was about 12 times greater than adsorption per gram of kaolinite.

Adsorption of desoxyribonucleic acid and protamine nucleate by bentonite was determined. Suspensions of coarse bentonite in *M* NaCl were mixed with solutions of the nucleic acid materials in *M* NaCl and *M* acetate buffer solutions at different pH values, and adsorption was measured. The adsorption behavior of both desoxyribonucleic acid and protamine nucleate was similar in nature and degree to adsorption of ribonucleic acid by bentonite in presence of water, sodium acetate, or NaCl.

Potentially cationic organic substances, such as proteins, are adsorbed more

strongly by clays under acid conditions than under neutral conditions (8). Nucleic acid materials, which contain cationic purine and pyrimidine groups, were also adsorbed to a greater degree by clays as the pH values of the suspensions decreased. The cationic portions of the nucleic acid materials are not the only groups, however, that could conceivably react with clays. Adsorption through the anionic orthophosphate groups might occur by any of the mechanisms of

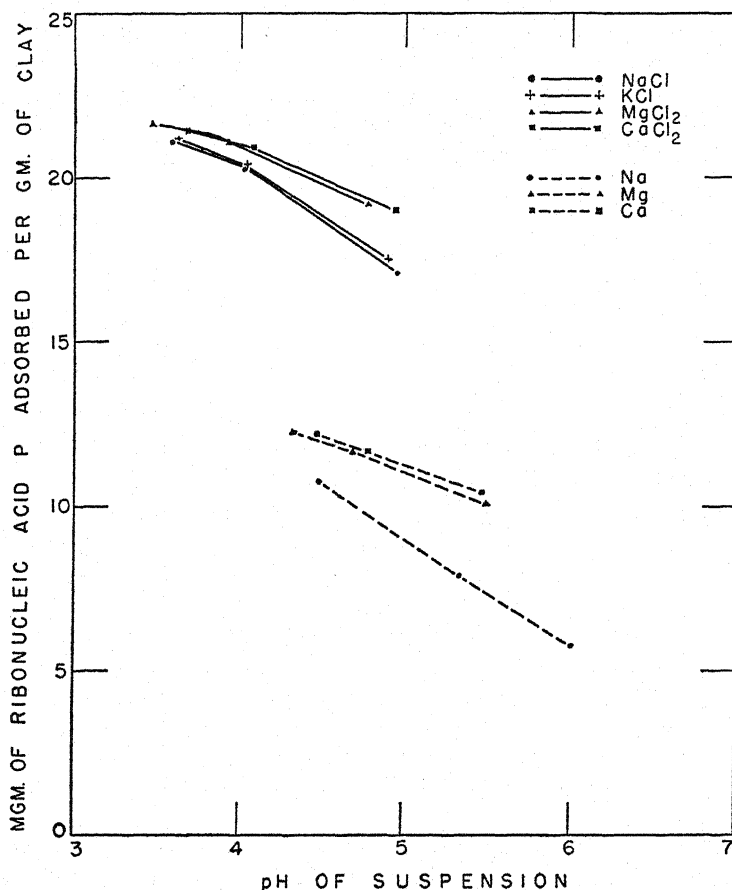


FIG. 2. ADSORPTION OF RIBONUCLEIC ACID BY COARSE BENTONITE IN PRESENCE OF SODIUM, POTASSIUM, CALCIUM, AND MAGNESIUM

fixation reviewed by Dean (5). Furthermore, the size of the organic molecule might also be a factor in adsorption, since mononucleotides were adsorbed to a lesser degree by the clays than were nucleic acids or protamine nucleate.

Reversibility of the reaction between ribonucleic acid and coarse bentonite. The previous experiments showed that the initial reaction between ribonucleic acid and bentonite approached equilibrium rapidly, and that the amount of adsorption at equilibrium was a function of many factors. The nature of adsorption was

further clarified by determining (a) whether equilibrium adsorption was constant for a specific mixture of ribonucleic acid, coarse bentonite, and NaOH even though the components of this mixture were allowed to react together in several different ways, and (b) whether the ribonucleic acid-bentonite complex could be dissociated as rapidly as it formed.

Equal amounts of ribonucleic acid were mixed for 24 hours with equal amounts of coarse bentonite differing only in NaOH content. Bentonite aliquots, equal to the initial bentonite aliquots, were then added to each mixture. The NaOH concentrations in the second bentonite aliquots were adjusted in such a way that the NaOH concentrations in the combined suspensions were the same. The combined suspensions were then shaken for an additional 96 hours, and analyses were made for adsorption. Adsorption of ribonucleic acid by bentonite was about the same in all instances, although the composition of the combined suspensions was obtained in several different ways.

In a second experiment, suspensions containing coarse bentonite, ribonucleic acid, and NaOH were mixed for 24 hours and then diluted with equal volumes of water. After the diluted suspensions were mixed for additional periods of 24, 48, and 96 hours, adsorption of ribonucleic acid phosphorus in these suspensions was compared with adsorption for similar periods in suspensions of similar composition the components of which were diluted with water before being mixed. Although after 24 hours there was greater adsorption in the former suspensions than in the latter, after 120 hours adsorption was about the same in all the suspensions.

These two experiments indicated that equilibrium adsorption was constant for a given mixture even though its composition might have been achieved in several different ways.

Experiments were also conducted to determine the facility with which ribonucleic acid could be removed from bentonite. Mixtures of 0.3 mgm. of ribonucleic acid phosphorus in solution and 10 mgm. of coarse bentonite in suspension were shaken for 24 hours. After centrifugation and decantation of the supernatant liquid, the residues were washed once with distilled water. They contained an average of 0.175 ± 0.004 mgm. of phosphorus. With three 10-ml. portions of the appropriate extracting solution, each residue was extracted for 10, 60 and 90 minute periods, and the amounts of phosphorus extracted by the solutions were measured. The results are shown in table 2.

The first extraction with the solutions having pH values above 8 removed more than 90 per cent of the ribonucleic acid phosphorus adsorbed by the clay, and the two subsequent extractions removed virtually all of the rest. Water and NaCl extracted only small portions of ribonucleic acid phosphorus. The amounts removed increased with an increase in the time of contact of the extracting solutions with the residue. Sodium chloride removed less ribonucleic acid than did water perhaps because the pH values in the former suspensions were lower than in the latter. Hydrochloric acid removed much more ribonucleic acid than did either water or NaCl but no so much as did the alkaline extracting solutions.

The periods of extraction in the previous experiment were probably not long enough to allow the suspensions to reach equilibrium. In measuring equilibrium adsorption, 0.242-mgm. quantities of ribonucleic acid phosphorus were added to 10-mgm. quantities of coarse bentonite, and the mixtures were shaken for 24 hours. Excess ribonucleic acid was removed by centrifugation, decantation, and washing of the residues with distilled water. The clay adsorbed an average of 0.143 ± 0.003 mgm. of ribonucleic acid phosphorus. The residues were suspended and shaken in the extracting solutions for varying periods, and the

TABLE 2
Extraction of ribonucleic acid phosphorus adsorbed by coarse bentonite

EXTRACTING SOLUTION	PH OF EXTRACTING SOLUTION	ADSORBED P EXTRACTED IN INDICATED PERIOD			ADSORBED P NOT EXTRACTED
		0-10 minutes	10-70 minutes	70-160 minutes	
		per cent	per cent	per cent	per cent
1 N HCl.....	0.2	19.2	50.0	18.0	12.8
Distilled water.....	6.0	6.4	11.7	11.1	70.8
1 M NaCl.....	6.0	5.1	6.8	10.2	77.9
0.2 M boric acid plus 0.05 N NaOH..	8.4	93.2	4.0	0.6	2.2
0.1 N Na ₂ CO ₃ plus 0.1 N NaHCO ₃ ...	9.5	94.8	4.0	0.6	0.6
0.05 M boric acid plus 0.05 N NaOH.	10.0	92.7	5.6	0.6	1.1
0.1 N Na ₂ CO ₃	11.1	92.7	5.6	0.6	1.1
1 N NH ₄ OH.....	11.8	94.3	4.0	0.6	1.1

TABLE 3
Equilibrium adsorption following treatment of ribonucleic acid-bentonite complex with different extracting solutions

EXTRACTION PERIOD	ADSORBED P NOT EXTRACTED BY INDICATED SOLUTIONS		
	1 N HCl	Distilled water	1 M NaCl
hours	per cent	per cent	per cent
1	49.0	92.2	95.2
6	30.2	88.6	91.6
24	15.6	88.7	91.7
72	14.3	—	—

phosphorus in solution was determined after each period. The results are shown in table 3.

Equilibrium adsorption of ribonucleic acid was approached within 6 hours with water and NaCl as the extracting solutions, and within 24 hours with HCl. Equilibrium adsorption with water as the extracting solution was about equal to equilibrium adsorption when the same total amounts of ribonucleic acid and bentonite were mixed and allowed to react together for 72 hours.

The evidence presented has shown that the reactions between ribonucleic acid and bentonite were readily reversible. The bentonite-ribonucleic-acid com-

plex was rapidly dissociated to different degrees by several acid solutions and was almost completely dissociated by alkaline solutions above pH 8.

Adsorption of ribonucleic acid by coarse and fine fractions of the clays. Large differences in equilibrium adsorption of ribonucleic acid by coarse fractions of bentonite, illite, and kaolinite were observed in previous experiments. The relation between equilibrium adsorption of ribonucleic acid and the cation-exchange capacities of coarse and fine clay fractions was studied in the following experiment. Suspensions containing 0.05 per cent H-bentonite, 0.25 per cent H-illite, and 0.25 per cent H-kaolinite were employed. Bentonite was suspended in 1 *N* NaCl, illite in 0.1 *N* NaCl, and kaolinite in 0.1 *N* NaCl. The total concentration of ribonucleic acid phosphorus in the suspensions was 0.015 mgm. per milliliter. The mixtures were allowed to react together for 24 hours, and adsorption of ribonucleic acid phosphorus was measured. The results are listed in table 4.

TABLE 4
Adsorption of ribonucleic acid phosphorus by size fractions of H-clays

CLAY	CATION- EXCHANGE CAPACITY PER 100 GM. CLAY	PH OF SUSPENSION	ADSORPTION OF P PER GM. OF CLAY	CATION- EXCHANGE CAPACITY ADSORPTION PER GM. OF CLAY
	<i>mc.</i>		<i>mgm.</i>	
Coarse fractions				
H-bentonite.....	83.0	3.77	20.30	4.09
H-illite.....	23.7	4.02	4.03	5.88
H-kaolinite.....	6.0	3.87	1.36	4.41
Fine fractions				
H-bentonite.....	89.0	3.61	20.80	4.28
H-illite.....	31.2	3.90	4.61	6.76
H-kaolinite.....	22.4	3.89	3.71	6.04

The fine clay fractions adsorbed more phosphorus per gram of clay than did the coarse clay fractions. The kaolinite fractions exhibited the most striking difference. There seemed to be a roughly linear relationship between the cation-exchange capacities of the clay fractions and adsorption of ribonucleic acid phosphorus.

Cleavage spacings of untreated coarse bentonite and of coarse bentonite on which nucleic acid materials were adsorbed. Organic molecules adsorbed between the silicate layers of bentonite will increase the cleavage spacings (10, 13). Adsorption of nucleic acid materials might also increase the distances between the silicate layers of the clay.

Samples of untreated coarse H-bentonite and coarse H-bentonite on which nucleic acid materials were adsorbed were washed with acetone and dried at 90°C. X-ray powder pictures were taken of the samples, nickel filtered radiation from a copper target and a plate distance of approximately 20 cm. being used. Cleavage spacings were calculated. The results are recorded in table 5.

Adsorption of any of the nucleic acid materials increased the spacing of the cleavage plane of the bentonite fraction. Thus the materials were at least partly adsorbed between the silicate layers of the clay.

Role of the cationic groups

Strong cationic groups of organic substances are readily adsorbed by clays (10). Nucleic acid materials contain weak cationic groups (3) and anionic orthophosphate groups that might be strongly adsorbed by clays (5). Nevertheless, the linear relation between the base exchange capacities of the clays and adsorption of ribonucleic acid was indirect evidence that the cationic groups were

TABLE 5

Cleavage spacings of untreated coarse bentonite and of coarse bentonite on which nucleic acid materials were adsorbed

NUCLEIC ACID MATERIAL	ORGANIC P ADSORBED PER GM. OF CLAY	SPACING OF CLEAVAGE PLANE
	mgm.	A.
None.....	—	13.5
Ribonucleic acid.....	8.6	14.4
Ribonucleic acid.....	24.0	18.3
Desoxyribonucleic acid.....	15.0	15.8
Protamine nucleate.....	—	17.5

TABLE 6

Adsorption of ribonucleic acid by coarse bentonite in absence and presence of amino acetic acid and arginine

pH OF SUSPENSION	ADSORPTION OF RIBONUCLEIC ACID P PER GRAM OF BENTONITE IN PRESENCE OF AMINO ACID INDICATED		
	None	Amino acetic	Arginine
	mgm.	mgm.	mgm.
4.15	18.1	15.5	15.1
5.10	10.7	8.4	8.4

adsorbed. The role of the cationic groups was further evaluated in several experiments.

Adsorption of ribonucleic acid by coarse bentonite in presence of proteins and amino acids. Adsorption of ribonucleic acid by bentonite in presence of other organic substances containing cationic groups was measured. Gelatin reduced the adsorption. This could have been caused not only by competition for the cation-exchange sites on the surface of the clay, but also by combination of the gelatin and ribonucleic acid molecules in solution, or by mechanical obstruction of adsorption of the smaller ribonucleic acid molecules by the larger gelatin molecules. The last two reactions were minimized by use of amino acetic acid and arginine instead of gelatin. The concentration of ribonucleic acid phosphorus was 0.015 mgm. per milliliter; of coarse H-bentonite, 005 per cent; of each amino

acid, 0.025 *M*; and of sodium acetate buffer, 1 *M*. Adsorption was measured after the suspensions were mixed for 24 hours. The results are shown in table 6.

Amino acetic acid and arginine decreased adsorption of ribonucleic acid by bentonite, probably by competition with ribonucleic acid for the cation-exchange sites on the surfaces of the clay.

Adsorption of untreated and deaminated ribonucleic acid by coarse bentonite. The hypothesis that the cationic groups of nucleic acid materials are adsorbed by clays was also tested by measuring adsorption of untreated and deaminated ribonucleic acid by coarse bentonite.

Partial removal of the amino groups of ribonucleic acid was accomplished by treating the material with a concentrated solution of NaNO_2 in glacial acetic acid for 24 hours at 25°C. (1). After mixture of 0.05 per cent suspensions of coarse H-bentonite, containing 0.015 mgm. of ribonucleic acid phosphorus per milliliter, and 2 *M* sodium acetate buffers for 24 hours, adsorption was measured. The results are shown in table 7.

TABLE 7

Adsorption of untreated and of deaminated ribonucleic acid by coarse bentonite

RIBONUCLEIC ACID PREPARATION	RIBONUCLEIC ACID P ADSORBED PER GM. OF CLAY	
	pH 4.18	pH 5.18
	mgm.	mgm.
Untreated.....	13.5	8.3
Deaminated.....	11.5	2.5

Less deaminated ribonucleic acid than untreated ribonucleic acid was adsorbed per gram of clay. Presumably, reduction of the cationic groups of the ribonucleic acid by deamination reduced the adsorption by bentonite.

The previous experiments indicated that the cationic groups of nucleic acid materials were adsorbed by clays. It remained to be shown whether the orthophosphate groups were also adsorbed.

Role of the phosphate groups

There was some evidence to show that the phosphate groups of nucleic acid materials were involved in adsorption. Adsorption of ribonucleic acid by clays was greater in presence of calcium or magnesium than in presence of sodium or potassium. Inorganic phosphate and carbohydrate phosphates were adsorbed by bentonite to a greater extent in presence of calcium than in presence of sodium (5, 12). By analogy, there was reason to presume that the phosphate groups of ribonucleic acid reacted with clays. The role of the phosphate groups was considered in several other experiments.

Inositol phosphates do not contain cationic groups but do contain orthophosphate groups. They were found to compete with inorganic phosphate for the phosphate-fixing sites of clays. It was also observed that adsorption of inositol phosphates by kaolinite or bentonite reduced subsequent adsorption of ribo-

nucleic acid. Conversely, adsorption of the latter compound reduced subsequent adsorption of the former compounds. Inositol phosphates and ribonucleic acid may have competed for the phosphate-fixing sites of the clays.

Citrate decreases adsorption of orthophosphate groups by bentonite.⁸ Except by mechanical obstruction, it should not interfere with adsorption of cationic organic groups by clays. Two experiments were conducted to test the effect of citrate on the adsorption of nucleic acid materials and inositol phosphates by clays.

In the first experiment, adsorption of ribonucleic acid, guanylic acid, and inositol phosphates by a natural kaolinite⁹ and coarse bentonite was measured in absence and presence of citrate. The concentration of ribonucleic acid phosphorus was 0.02 mgm. per milliliter and of guanylic acid and inositol phosphate phosphorus 0.01 mgm. The concentration of kaolinite was 2.0 per cent and of bentonite 0.1 per cent. The clays and organic phosphorus compounds were mixed in *M* ammonium acetate (pH 4.3) with and without 0.1 *M* ammonium citrate

TABLE 8

Adsorption of ribonucleic acid, guanylic acid, and inositol phosphates by kaolinite and bentonite in presence and absence of citrate

ORGANIC PHOSPHORUS COMPOUND	P ADSORBED PER GM. OF CLAY WITH CITRATE PRESENT		P ADSORBED PER GM. OF CLAY WITH CITRATE ABSENT	
	Kaolinite	Bentonite	Kaolinite	Bentonite
	mgm.	mgm.	mgm.	mgm.
Ribonucleic acid.....	0.085	6.27	0.556	14.27
Guanylic acid.....	0.001	0.14	0.120	1.77
Inositol phosphates.....	0.013	0.24	0.488	9.62

(pH 4.3). The mixtures were shaken for 24 hours, and adsorption of phosphorus by the clays was measured. The results are shown in table 8.

In the second experiment, 2-gm. samples of coarse kaolinite and 1-gm. samples of coarse bentonite were extracted twice with 40-ml. quantities of 0.5 *M* ammonium acetate (pH 4.3) or 0.5 *M* ammonium acetate containing 0.1 *M* ammonium citrate (pH 4.3). The citrate-treated clays were then extracted three times with 0.5 *M* ammonium acetate to remove citrate. The clays not treated with citrate were extracted in the same manner. In an independent experiment, it was found that citrate could be removed from clays by repeated extraction, and that the traces of citrate that could remain would not appreciably influence adsorption of organic phosphates. The amounts of iron and aluminum in the acetate and the acetate plus citrate extracts were determined. The treated and untreated clays were suspended in *M* ammonium acetate (pH 4.0), mixed with inositol phosphates and ribonucleic acid, and adsorption of phosphorus was determined after shaking for 24 hours. The concentration of kaolinite was 2.0

⁸ Goring, C. A. I. Reactions of biological organic phosphorus compounds with clays. 1950. [Unpublished Ph. D. thesis. Copy on file Iowa State Col. Library, Ames]

⁹ This natural kaolinite has been described fully by Low and Black (14).

per cent, of bentonite 0.1 per cent, of ribonucleic acid phosphorus 0.02 mgm. per milliliter, and of inositol phosphate phosphorus 0.01 mgm. per milliliter. The results are shown in table 9.

Table 8 shows that citrate decreased adsorption of the organic phosphorus compounds by the clays. The effect of citrate on adsorption of guanylic and ribonucleic acids by kaolinite was relatively greater than its effect on adsorption by bentonite, but its effect on adsorption of inositol phosphates was about the same with both clays.

Citrate could have decreased adsorption in four ways. It could have (a) decomposed appreciable amounts of the clays, (b) detached phosphate-fixing elements from the clays, (c) chemically or (d) mechanically obstructed adsorption by becoming attached to the phosphate-fixing sites of the clays.

Decomposition of the clays need not be considered, because in both experiments more than 97 per cent of the clays were recovered. Because the cationic groups of nucleic acid materials are adsorbed by clay, citrate anions could com-

TABLE 9

Iron and aluminum extracted by treatment of clays with ammonium acetate and ammonium citrate, and adsorption of organic phosphates by treated and untreated clays

EXTRACTING SOLUTION	Fe EXTRACTED PER GM. OF CLAY		Al EXTRACTED PER GM. OF CLAY		P ADSORBED PER GM. OF KAOLINITE		P ADSORBED PER GM. OF BENTONITE	
	Bentonite	Kaolinite	Ben- tonite	Kao- linite	Ribo- nucleic acid	Inositol phos- phates	Ribo- nucleic acid	Inositol phos- phates
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
None.....	—	—	—	—	0.332	0.490	9.40	9.60
Ammonium acetate.....	0.0546	0.0124	4.180	0.485	0.258	0.291	5.56	1.38
Ammonium acetate plus ammonium citrate.....	0.2340	0.0525	5.100	0.519	0.229	0.226	4.24	0.27

pletely prevent adsorption of these materials only by forming a perfect mechanical barrier between the anionic sites of the clay mineral and the cationic groups. Citrate reduced adsorption of the nucleic acid materials by kaolinite to almost negligible amounts and, therefore, must have formed a mechanical barrier on the surface of kaolinite. It considerably reduced adsorption of nucleic acid materials by bentonite and, thus, might have acted to some extent as a mechanical barrier on the surface of bentonite. It might also have reduced adsorption by competing with the nucleic acid materials for phosphate-fixing sites, or by detaching phosphate-fixing elements from the clays. Adsorption of inositol phosphates was almost completely prevented by one or both of these mechanisms.

Table 9 shows that extraction of the clays with acetate or with acetate plus citrate substantially decreased adsorption of organic phosphorus. It has already been shown that adsorption was not appreciably decreased by suspending untreated clays in acetate, but was appreciably decreased by suspending them in acetate plus citrate. Presumably, repeated washings of the clays with acetate may dissolve appreciable amounts of the phosphate-fixing elements, but citrate

merely in contact with the clays will combine with or detach almost all of the phosphate-fixing elements. Less than half of the phosphate-fixing elements of kaolinite, but almost all of bentonite, were detached by acetate plus citrate, as shown by adsorption of inositol phosphates (table 9). In contrast, adsorption of ribonucleic acid by bentonite was reduced by only 55 per cent, again showing that the cationic groups of nucleic acid materials were adsorbed by clays. Extraction with citrate did not substantially decrease the cation-exchange capacity of bentonite. In an independent experiment, the cation-exchange capacity of bentonite repeatedly washed with 0.1 *M* citric acid was reduced from 83 to 77 me. per 100 gm. of clay, but its ability to adsorb ribonucleic acid was reduced by 53 per cent.

Table 9 also shows that appreciable amounts of aluminum and much smaller amounts of iron were removed from the clays. About one tenth as much aluminum was removed from kaolinite as from bentonite. It has been argued that iron or aluminum on the surface of clay or as part of the clay lattice is responsible for phosphate fixation (5). In this experiment, aluminum seemed to be more important than iron. Not all the aluminum and iron removed from the clays would necessarily take part in adsorption, since there probably was slight decomposition of the clays. Nevertheless, the larger amounts of aluminum removed from bentonite as compared to kaolinite corresponded with a greater reduction in adsorption of inositol phosphates by the former clay.

In another experiment, natural and acid-washed kaolinite were extracted with citrate plus acetate. The reduction in adsorption of inositol phosphates by the former was less than by the latter. This difference may have been associated with the greater amounts of citrate-soluble aluminum on the surface of the acid-washed clay.

It was concluded that nucleic acid materials were adsorbed by clays through their cationic and orthophosphate groups. The orthophosphate groups were adsorbed on bentonite by elements easily detached by citrate, and those on kaolinite in part by easily detached elements and in part by more stable elements.

DISCUSSION

The results obtained in this study may be useful in understanding some phases of the biochemistry of soil organic phosphorus. Nucleic acid materials appear to be major organic phosphorus constituents of soils (2, 21). It was shown in this study that they are adsorbed to the greatest degree by clays between pH 0.1 and 4. Likewise, soil organic phosphorus was found to be least soluble between pH 2 and 4⁸. Adsorption of nucleic acid materials by clays decreases from pH 4 to 7 and is almost negligible above pH 8. Similarly, the solubility of soil organic phosphorus was found to increase slowly from pH 4 to 7 and rapidly above pH 7.⁸

Adsorption by clays or soils appears to influence the rate at which organic phosphorus is dephosphorylated. It has been observed that the reduction in dephosphorylation of nucleic acid materials or microbial organic phosphorus

corresponds with the degree to which these substances are adsorbed by clays (2, 11). Furthermore, the rate of dephosphorylation of nucleic acid added to soil was found to decrease with decreasing pH of the soil (2). These results correspond in principle with results obtained for mineralization of soil organic phosphorus. The percentage of the organic phosphorus mineralized in 25 days at 40°C. in soils below pH 6 was found to be less than in soils above pH 6.¹⁰ Furthermore, there was a highly significant negative correlation between pH and soil organic phosphorus content expressed as a percentage of the total phosphorus. Thus, the mineralization of soil organic phosphorus might depend, to a considerable degree, on the adsorption of nucleic acid materials by the clay minerals in soils.

SUMMARY AND CONCLUSIONS

The general nature of adsorption of nucleic acid materials by clays was studied. Adsorption was influenced by the reaction period, the temperature, the type and concentration of clay and nucleic acid material, the pH and the inorganic cation present.

The rate of reaction of ribonucleic acid with the clays was rapid, equilibrium being approached within 24 hours. Increasing the temperature from 7°C. to 45°C. increased the rate of reaction but did not influence equilibrium adsorption. Increasing the concentration of nucleic acid material and decreasing the pH or clay concentration, increased adsorption of phosphorus per gram of clay. The order of decreasing ability to adsorb was bentonite > illite > kaolinite, and to react, nucleic acids and protamine nucleate > mononucleotides. Adsorption of ribonucleic acid was greater in presence of calcium or magnesium than in presence of sodium or potassium. The reactions between ribonucleic acid and bentonite were found to be reversible. Adsorption of ribonucleic acid was linearly related to the cation-exchange capacities of coarse and fine fractions of the clays. With bentonite, the nucleic acid materials were at least partly adsorbed between the silicate layers.

The mechanism of adsorption of nucleic acid materials by clays was also studied. It was concluded that nucleic acid materials were adsorbed through their cationic and orthophosphate groups.

The relation between adsorption of nucleic acid materials by the clays and dephosphorylation of soil organic phosphorus was discussed.

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EFFECTS OF 2,4-D AND CADE, SINGLY AND IN COMBINATION, UPON NITRATE AND BACTERIAL CONTENT OF SOILS

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Received for publication September 17, 1951

In spraying for weed control the soil may be unavoidably contaminated or the herbicides may be introduced directly to its surface when pre-emergence spraying is employed. In either event, it is of interest to know the effects of these herbicides on biological processes in the soil.

Smith, Dawson, and Wenzel (12) observed no adverse effects on total plate counts or on the number of actinomyces, fungi, and protozoa in either sandy soil of good fertility or in silt loam when 2,4-dichlorophenoxyacetic acid (2,4-D) was applied at rates of 0.5 to 500 ppm. (1 to 1,000 pounds per acre). The nitrite- and nitrate-forming organisms in both soils were definitely injured by 100 ppm. (200 pounds per acre) but recovered in 10 to 40 days. The harmful effect upon nitrification was somewhat less marked in sandy soil. The nitrite-forming bacteria were more sensitive than the nitrate-forming bacteria. Newman and Norman (8, 9) reported that 2,4-D had no effect on the numbers of organisms present in the soil or on the nitrification process until the compound was added in great excess. They suggested that some soil microorganisms can probably use 2,4-D as a source of energy. Jones (4) found that under the conditions of his experiments, rates of 2,4-D up to 25 pounds per acre had no unfavorable effects on nitrate formation in a soil to which no nitrogen had been added. When nitrogen in the form of urea and sodium nitrate was added, there was an indication that 15 pounds per acre was sufficient to inhibit nitrate formation temporarily. The effect was more noticeable when sodium nitrate was added.

To the writers' knowledge there have been no publications on the effects of Concentrated Activated Diesel Emulsion (CADE)² and the combination of 2,4-D and CADE, herbicides widely employed in Hawaii, upon nitrate accumulation or total plate counts of bacteria in soil.

MATERIALS AND METHODS

The soils used were a cultivated sandy loam and a cultivated silt loam obtained from the vicinity of Manhattan, Kansas. Soil from the surface 6 inches was brought to the laboratory, air-dried, passed through a 2-mm. sieve, thoroughly mixed, and stored in a canvas bag. The sandy soil had a pH of about 7.2, a water-holding capacity of 40.6 ml. per 100 gm., and a nitrate-nitrogen content of ap-

¹ A cooperative investigation by the Kansas Agricultural Experiment Station and the Experiment Station of the Hawaiian Sugar Planters' Association. Contribution No. 270, department of bacteriology, Kansas Agricultural Experiment Station, and Journal Series No. 10, Experiment Station, Hawaiian Sugar Planters' Association, Honolulu.

² For a detailed discussion of the herbicide see Hance, F. E. Weed control on Hawaiian sugar-cane lands—contact herbicides. *Hawaii Planters' Rec.* 52(2): 93-112. 1948.

proximately 4.0 ppm.; the silt loam a pH of 6.5, a water-holding capacity of 47 ml., and a nitrate-nitrogen content of approximately 2.0 ppm.

To 100-gm. portions of soil (oven-dried basis) was added 100 ppm. of nitrogen as $(\text{NH}_4)_2\text{SO}_4$, and after thorough mixing the portions were placed in 350-ml. wide-mouth bottles.

The herbicides studied were supplied by the Experiment Station of the Hawaiian Sugar Planters' Association and included the following:

1. Hawaiian Sugar Planters' Association 2,4-D magma³ containing 30 per cent by weight of 2,4-D which had been converted to the normal sodium salt by treatment with Na_2CO_3 . This nitrogen-free, water-soluble agent was dissolved at the rate of 0.25 pound of 2,4-D per gallon. The resulting solution with a pH of about 7.5 was labeled the "blanda" solution and was used in making up the combination of 2,4-D and CADE.

2. CADE containing 67 per cent diesel oil and 33 per cent pentachlorophenoate. A definite amount of a stock solution of the activator (SSA) was added to the final dilution of 1 part of CADE to 16 parts of water before use in these studies. The SSA contained 6 parts of H. S. P. A. Activator (sodium pentachlorophenate, U. S. patent No. 2,370,349) and 1 part of 2-7R⁴ in water. The mixture employed was of the following composition: 145 ml. of distilled water, 5 ml. of SSA, and 10 ml. of CADE.

3. 2,4-D in combination with CADE to which was added a definite quantity of SSA. The final mixture of these two herbicides included the ingredients in the following proportions: 400 ml. of "blanda" solution, 445 ml. of distilled water, 5 ml. of 2-7R, 50 ml. of SSA, and 100 ml. of CADE.

The herbicides were applied to the soil in sufficient volumes of water to bring the soil up to 50 per cent of its water-holding capacity. The bottles were stoppered tightly with cotton to reduce water loss and incubated at room temperature in the dark. The desired moisture level was maintained by adding distilled water every 6 to 8 days. At intervals of a few days all germinating weed seedlings were either pinched off at the level of the soil surface or pulled out to prevent measurable loss of nitrate nitrogen due to utilization by the growing plants.

Triplicate samples of each treatment were extracted for nitrate nitrogen at intervals of 0, 2, 4, 8, and 16 weeks, a dilution of three parts of distilled water to one part of soil being used. Duplicate 10-ml. aliquots were evaporated over steam, thus giving a total of six replications for each herbicidal concentration. Nitrate nitrogen was determined by the phenoldisulfonic acid method as described by Schreiner and Failyer (11) and modified by Lipman and Sharp (5). The Duboscq colorimeter was utilized for all colorimetric readings.

A preliminary test run to determine whether the herbicides employed in these studies interfered in any way with the phenoldisulfonic acid method indicated that they caused no irregularities in the results.

Where plate counts were made, 10-ml. samples were removed from the soil extraction suspension, after shaking but prior to addition of the flocculating agent, from which serial dilutions were prepared. Egg-albumin agar adjusted to pH 7.2 and of the following composition was used as a plating medium: 1.0 gm. glucose, 0.25 gm. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.50 gm. K_2HPO_4 , trace $\text{Fe}_2(\text{SO}_4)_3$, 0.50 gm. yeast extract, 20.0 gm. agar-agar, 0.25 gm. egg albumin, and 1,000 ml.

³ Reference is made to the pasty state of the chemical.

⁴ A water-soluble sulfonated aromatic paste used as a wetting agent.

distilled water. Five plates were poured for each concentration of the herbicides. A dilution of 1 to 100,000 was found most favorable. The plates were incubated for 5 days at room temperature before counts were made. Longer incubation was unwise because of the rapid growth of spreading colonies.

RESULTS

Experiment 1. Effects of herbicides on nitrate accumulation in sandy loam. The results of this experiment are presented in table 1. The sodium salt of 2,4-D applied directly to the soil at rates of 3 (ordinary field application) and 10 pounds

TABLE 1

Effects of 2,4-D, CADE, and a combination of 2,4-D and CADE upon nitrate accumulation in sandy loam

TREATMENT		NH ₂ -N ADDED	NO ₃ -N IN SOIL AFTER INCUBATION					WEED SEEDS GERMI- NATING
Herbicide	Rate per A.		0 weeks	2 weeks	4 weeks	8 weeks	16 weeks	
		<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>	
2,4-D	0 lb.	100	4.5	59.7	97.6	98.6		92
2,4-D	1 lb.	100	4.6	57.4	97.6	112.1		48
2,4-D	3 lb.	100	4.5	47.5*	80.5†	105.3		14
2,4-D	10 lb.	100	4.2	47.0*	66.0†	101.2		11
2,4-D	25 lb.	100	4.2	35.3†	65.1†	97.6		1
2,4-D	50 lb.	100	4.4	35.3†	58.3†	97.6		0
CADE	0 gal.	100	4.3	64.2	97.6	99.4	130.2	73
CADE	10 gal.	100	4.5	57.4*	97.6	101.2	130.2	95
CADE	100 gal.	100	4.1	58.8	97.6	99.4	135.6	84
CADE	500 gal.	100	4.5	27.3†	67.3†	97.6	130.2	37
CADE	5000 gal.	100	4.2	7.7†	9.5†	14.0†	23.5†	0
2,4-D + CADE	0 gal.	100	3.5	59.7	97.6	108.5	172.7	100
2,4-D + CADE	3 gal.	100	3.4	59.7	97.6	108.5	172.7	96
2,4-D + CADE	30 gal.	100	3.5	59.7	97.6	108.5	177.2	94
2,4-D + CADE	100 gal.	100	3.4	42.5†	82.7†	108.5	172.7	19
2,4-D + CADE	1000 gal.	100	2.7	7.2†	20.1†	40.7†	108.5†	0

* Significant reduction.

† Highly significant reduction.

per acre, brought about statistically significant reduction in nitrate accumulation during the 0-2-week interval and highly significant reduction during the 2-4-week interval. The higher rates of 25 and 50 pounds caused a highly significant diminution in nitrate accumulation during the 0-4-week interval. Nevertheless, in every case where reduced nitrate formation was evident during the first 4 weeks the total amount of nitrate nitrogen accumulating during the 8 weeks was, for practical purposes, the same as in untreated controls.

CADE is usually applied at a rate of 100 gallons per acre in the drier sections of the sugar plantations and at a rate of 500 gallons in areas of plentiful rainfall. At the lower rate this herbicide caused no significant reductions in total nitrates formed during the periods tested. At the higher rate a highly significant reduc-

tion was noticeable throughout the first 4 weeks. A marked reduction in total nitrates was evident throughout the 16 weeks at the 5,000-gallon rate.

The combination of the herbicides (2,4-D + CADE) caused no reductions in nitrate accumulation when applied at the usual field rate of 30 gallons per acre or less. A highly significant reduction persisted for 4 weeks following the 100-gallon application, and a still greater reduction was noticeable throughout the 16-week period where the herbicide was applied at 1,000 gallons.

TABLE 2

Effects of 2,4-D, CADE, and a combination of 2,4-D and CADE upon nitrate accumulation in silt loam

TREATMENT		NH ₄ -N ADDED	NO ₃ -N IN SOIL AFTER INCUBATION*			
Herbicide	Rate per A.		2 weeks	4 weeks	8 weeks	16 weeks
		ppm.	ppm.	ppm.	ppm.	ppm.
2,4-D	0 lb.	0	13.6	20.3	30.7	47.0
2,4-D	0 lb.	100	29.8	59.7	101.7	143.7
2,4-D	1 lb.	100	28.0	59.7	101.7	143.7
2,4-D	3 lb.	100	26.2	59.7	101.7	143.7
2,4-D	10 lb.	100	21.7†	46.1†	89.5†	134.2
2,4-D	25 lb.	100	14.5†	31.6†	61.0†	103.1†
2,4-D	50 lb.	100	12.2†	19.0†	35.3†	50.6†
CADE	0 gal.	0	13.6	20.3	32.5	46.1
CADE	0 gal.	100	38.0	78.7	107.1	134.2
CADE	100 gal.	100	34.5	67.8†	101.7	134.2
CADE	500 gal.	100	32.5†	54.2	97.6	128.8
CADE	1000 gal.	100	24.4†	46.1†	93.7	112.5†
CADE	5000 gal.	100	10.8†	18.5†	32.5†	61.5†
2,4-D + CADE	0 gal.	0	12.7	20.3	25.3	47.0
2,4-D + CADE	0 gal.	100	35.3	65.1	86.8	128.8
2,4-D + CADE	30 gal.	100	33.4	59.7	89.5	134.2
2,4-D + CADE	50 gal.	100	26.2†	58.8	88.1	134.2
2,4-D + CADE	100 gal.	100	25.8†	56.0†	89.5	128.8
2,4-D + CADE	1000 gal.	100	9.3†	17.4†	28.0†	51.5†

* The initial NO₃-N content was 1.9 ppm.

† Significant reduction.

‡ Highly significant reduction.

The data in table 1 show that 2,4-D even at the rate of 1 pound per acre, retarded germination of weed seeds. At higher rates the retardation was more marked, germination being completely inhibited at the 50-pound application.

CADE did not retard weed seed germination at rates of 100 gallons per acre or less. A marked inhibition was noticeable at 500 gallons, and complete inhibition of germination was observed at 5,000 gallons.

The combination of the two herbicides failed to retard weed seed germination at the usual field rate of 30 gallons per acre or less. Marked inhibition was noticeable at 100 gallons and inhibition was complete at 1,000 gallons.

Experiment 2. Effects of herbicides on nitrate accumulation and total plate counts

in silt loam. Results of this experiment are presented in table 2. In this silt loam soil 2,4-D applied at the usual field rate of 3 pounds per acre or less did not cause a significant reduction in nitrate accumulation during 16 weeks. With applications of 10 and 25 pounds per acre, highly significant reductions in nitrate accumulation were evident throughout the first 8 weeks. The rates of accumulation during the 8- to 16-week interval following these treatments were equal to those of the controls, even though the total quantities of nitrate present at 16 weeks were somewhat less. A more marked reduction in nitrification was caused by the 50 pound application and persisted throughout the 16 weeks.

TABLE 3

Effects of 2,4-D, CADE, and a combination of 2,4-D and CADE upon the total plate counts in silt loam

TREATMENT		BACTERIA IN MILLIONS PER GRAM AT DIFFERENT PERIODS AFTER TREATMENT*			
Herbicide	Rate per A.	2 weeks	4 weeks	8 weeks	16 weeks
2,4-D	0 lb.	6.7	3.1	5.6	2.0
2,4-D	1 lb.	5.2	5.1	3.3	2.0
2,4-D	3 lb.	4.6	6.5	3.3	1.3
2,4-D	10 lb.	7.1	6.3	2.2	2.2
2,4-D	25 lb.	13.0	10.4	7.5	3.5
2,4-D	50 lb.	13.4	11.0	7.8	2.0
CADE	0 gal.	3.7	5.0	4.0	3.5
CADE	100 gal.	8.6	12.6	5.9	4.0
CADE	500 gal.	13.3	16.3	10.2	2.8
CADE	1000 gal.	26.7	25.9	5.5	3.6
CADE	5000 gal.	30.4	29.5	11.5	6.5
2,4-D + CADE	0 gal.	3.3	5.1	3.1	1.8
2,4-D + CADE	30 gal.	2.1	6.4	4.3	2.1
2,4-D + CADE	50 gal.	8.1	5.7	5.1	2.7
2,4-D + CADE	100 gal.	8.8	8.0	4.0	3.2
2,4-D + CADE	1000 gal.	22.6	23.2	18.9	15.2

* The initial bacterial count was 5.1 millions.

CADE applied at rates up to 1,000 gallons per acre caused highly significant reductions in nitrification only during the first 4 weeks. When CADE was applied at the rate of 5,000 gallons, formation of nitrate was highly significantly reduced during the first 8 weeks; however, the rate of formation during the last 8 weeks was equal to that in the controls, indicating complete recovery of the nitrifying organisms, even though the total nitrate content in this sample at 16 weeks was less than half that in the untreated control.

As in the sandy loam soil, the combination of the two herbicides when applied to the soil at rates up to 100 gallons per acre did not cause any reduction in total nitrate accumulation during the 16 weeks, though at 50 and 100 gallons a highly significant retardation in nitrification was evident during the first 2 weeks. An application of 1,000 gallons per acre invariably caused a highly significant reduction in nitrate formation which persisted through the test period.

Data on the influence of the herbicides upon the total plate counts in the silt loam are presented in table 3.

These data indicate that 2,4-D, CADE, or a combination of the two, when applied to this particular soil in the concentrations ordinarily employed, exerted no appreciable influence upon the bacterial plate counts. However, 2,4-D in concentrations of 25 pounds per acre or higher, CADE in concentrations of 500 gallons or more, and a combination of the two in concentrations of 1,000 gallons or more resulted in temporary increases in the plate counts, the magnitude and duration of the increase in bacterial populations increasing as the quantity of herbicides increased.

TABLE 4
Initial effect of 2,4-D, CADE, and 2,4-D + CADE on bacterial numbers in sandy loam

TREATMENT		BACTERIA IN MILLIONS PER GRAM AT DIFFERENT PERIODS AFTER TREATMENT*				
Herbicide	Rate per A.	3 hr.	6 hr.	24 hr.	7 days	14 days
0	0 gal.	43.4	53.0	66.8	75.8	31.8
2,4-D	50 lb.	69.2	53.3	49.2	69.3	32.7
CADE	5000 gal.	19.5	12.8	48.4	183.4	207.2
2,4-D + CADE	1000 gal.	28.2	28.4	30.4	143.7	172.4

* The initial bacterial count was 47.4 million.

Experiment 3. Effects of herbicides on bacterial numbers in sandy loam. The data relative to the influence of herbicides upon bacterial numbers in the preceding experiment suggested the possibility that the herbicides might be functioning as agents bringing about the well-known partial sterilization phenomena. To gain more specific information on this point, experiment 3 was carried out. This experiment was set up in the same general manner as the preceding experiments except that fresh undesiccated sandy loam soil was employed and a single concentration of the various herbicides, presumably high enough to be effective, was employed. To detect an initial sterilizing effect, the time intervals for analysis were reduced to hours and days instead of weeks (table 4).

These data indicate that 2,4-D did not function as a sterilizing agent in this soil, and neither was there any marked increase in bacterial numbers following treatment up to 50 pounds per acre. On the other hand, CADE temporarily reduced the bacterial population developing on poured plates. This reduction was followed by marked increases in the bacterial flora within 7 to 14 days. Thus, the over-all bacterial population curve paralleled that following the application of any volatile disinfectant. Time did not permit a careful study of other partial sterilization phenomena.

DISCUSSION OF RESULTS

The toxicity to vegetation of the three herbicides used in these studies was demonstrated by the marked inhibition of the germination of various weed seeds in the soil; this was especially noticeable at the higher concentrations.

The toxicity of 2,4-D to various soil microorganisms has been observed by several investigators and reviewed by Jones (4). The concentrations of 2,4-D recorded as toxic, however, have been far above those normally used in the control of weeds. Soil conditions have been reported as influencing to some extent the toxicity of the acid to soil microorganisms.

The data here reported relative to 2,4-D substantiate previous findings in that normal field applications were found to be without effect upon either the nitrifying bacteria or the plate counts. This was found to be true also of CADE and of the combination of 2,4-D and CADE. A temporary depression in the activity of the nitrifying bacteria became evident as the concentrations of all three herbicides were increased. Both the extent and the duration of this depressed nitrification increased as the concentration of the herbicide increased. In no instance, however, even with the highest concentration tested, was nitrification completely stopped. Furthermore, in all but three instances, namely, 50 pounds 2,4-D and 1,000 gallons 2,4-D + CADE per acre in the silt loam and 5,000 gallons CADE per acre in the sandy loam, normal nitrification was regained within 8 to 16 weeks even with the highest applications of all three herbicides.

In view of the large excess accumulation of nitrate nitrogen over the added ammonium nitrogen, it is also evident that the herbicides did not destroy the ability of the soil flora to mineralize the soil's store of organic nitrogen.

The fate of 2,4-D and CADE in soils is unknown. Neither is it known how the bacteriostatic action of these agents upon microorganisms is accomplished. Though high concentrations of CADE may bring about limited bactericidal action, the supposedly more delicate nitrifying organisms are not completely destroyed. In fact, appreciable formation of nitrates was taking place in the presence of the highest concentrations of the herbicides throughout the entire experimental period.

The herbicides under study are not volatile, and the experimental conditions prohibited leaching. The herbicide 2,4-D has been reported as disappearing from soils within a few weeks, and its disappearance has been associated with microbial activity. Several investigators have suggested utilization of the acid by various organisms (1, 2, 3, 6, 7, 9, and 10). Most of the evidence has been of an indirect nature. The time intervals suggested for the disappearance of 2,4-D from soils correspond more or less with the duration of the bacteriostatic effect upon nitrifying bacteria.

There are no reports available relative to the action of CADE upon microorganisms or its disappearance from soils. It is well known, however, that many simple and fairly complex hydrocarbons can be utilized by various types of widely distributed soil microorganisms, and it is conceivable that such organisms are responsible for the destruction of CADE and, hence, the elimination of its bacteriostatic effect. One observation in the silt loam soil is interesting in this connection; namely, that the accumulation of nitrate nitrogen in the samples receiving the heaviest application of the herbicides paralleled almost perfectly the accumulation of nitrates in the untreated control which received no ammo-

nium nitrogen. This suggests the possibility that the herbicides might, in some way, have temporarily immobilized the ammonium sulfate nitrogen. No explanation is available as to how this could have been accomplished. This problem is being investigated further.

SUMMARY

2,4-D, CADE, and the combination of 2,4-D and CADE applied to the sandy loam and silt loam soils at the usual field rates of 3 pounds, 100 and 500 gallons, and 30 gallons per acre, respectively, did not appreciably reduce the total nitrates that accumulated during the different intervals.

Although there were marked temporary reductions in the total nitrates accumulating in samples treated with high concentrations of the herbicides, the accumulation of nitrate nitrogen was not completely inhibited, and within 8 to 16 weeks the rate of accumulation in most instances had again reached that in untreated soils.

The higher concentrations of the herbicides applied to the soil samples caused a temporary increase in total plate counts as determined on egg albumin agar.

High concentrations of CADE and the combination of 2,4-D and CADE exhibited a typical partial sterilization phenomenon; 2,4-D alone at the rate of 50 pounds per acre did not exhibit a similar phenomenon.

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BOOKS

Agricultural Resources of China. By T. H. SHEN. Cornell University Press, Ithaca, N. Y., 1951. Pp. 407, figs. 20. Price \$5.

The author of this very interesting book points out that he is dealing with a land area that supports 450 million people, about one fifth of the population of the earth. The whole agricultural economy of the nation is discussed under headings of physiography, biological factors, water resources, economic factors, land use, food consumption, food crops, oil crops, tea, tobacco, livestock, fisheries, fibers, and forests, with some suggestions as to education, extension, and research for better utilization of agricultural resources. The animal population is estimated at 29 million cattle; 10 million horses, mules, and asses; 48 million pigs; and 21 million sheep and goats. The fertilizer program consists largely of canal mud, legume green manures, human excreta, estimated at 100 million metric tons annually, and animal manures, estimated at 400 million metric tons.

Les Cahiers de la Recherche Agronomique. Service de la Recherche Agronomique et de l'Expérimentation Agricole, Rabat, 1950. Pp. 479, paper-bound.

This report contains a detailed discussion and extended bibliography of the legume forage crops of Morocco by André Foury, shorter discussions of *Eragrostes* and *Melinis nimutiflora* by the same author, papers on *Panicum* and *Pennisetum* by Guy Perrin de Brichambaut, and a final paper on the millets by Marcel Niqueux. A large number of good illustrations are presented in the report.

Disease in Plants. By NEIL E. STEVENS AND RUSSELL B. STEVENS. The Chronica Botanica Co., Waltham, Mass., and Stechert-Hafner, Inc., New York, 1952. Pp. 219, figs. 61. Price \$4.75.

This is the first of a series of 12 volumes designated as a "Manual of Plant Sciences" that is being edited by Frans Verdoorn. It is an introduction to the science of agricultural phytopathology. The manuscript was essentially finished at the time of the senior author's death; his son was called on to complete the task. Following an interesting introduction, the authors deal with causal agents, factors influencing disease development, variation in plant pathogens, and disease control. Soil scientists will be specially interested in the chapters on nutritional factors, weather and soil, and soil treatment and crop rotation. Among the special features are several very attractive engravings, a page of quotations about disease from ancient writers, reproduction of the frontispiece of Father Zallinger's *De Morbis Plantarum*, layout of a classic set of experimental plots used by Tillet near Bordeaux, and Jacob Eriksson's plea for international collaboration in disease control. Reference is made to the work of some 300 authors. The book is a highly attractive and valuable addition to the literature.

Dynamique du Sol. Volume 1, Fifth Edition. By A. DEMOLON. Dunod, Paris, 1952. Pp. 520, figs. 132. Price 4,600 F.

The fourth edition of volume 2 of this set, entitled "Croissance des Végétaux

Cultivés," was published in 1950. This volume, as in the previous edition, is divided into four parts: evolution, physics, chemistry, and biology of soils. Considerable improvement has been effected in the presentation, and much new material has been reviewed. Specific references are given at the bottoms of the pages, and general references are shown at the end of each of the 17 chapters. The appendix gives methods of sampling and analyzing soils. The illustrations are largely graphs but include one plate of soil profiles in color. The book merits special consideration as a text for graduate students who want to increase their ability to read French. The author is an excellent writer, and the material is presented in an attractive and highly interesting form.

Farm Power. By BEN D. MOSES AND KENNETH R. FROST. John Wiley and Sons, Inc., New York, 1952. Pp. 484, figs. 285. Price \$5.75.

Almost every question one might have about internal combustion engines and tractors is answered in this well-developed and excellently illustrated volume that begins with a discussion of relation of farm power to agriculture and ends 34 chapters later with a list of good references. At the close of each chapter is a set of good questions and problems that are designed to fix the essential points in the student's mind. On completion of the course, the student should have a good understanding of carburetion, ignition, power transmission, power measurement, tractor equipment, traction, lubrication, and the economics of farm power. The authors have made a highly important contribution to the teaching literature in this field.

A Laboratory Manual for Soil Fertility Students. By DARRELL A. RUSSELL. Wm. C. Brown Company, Dubuque, Iowa, 1950. Pp. 75. Price, paper-bound, \$1.85.

This manual is designed for laboratory work in the beginning course in soil chemistry and fertility at the University of Illinois. The 13 exercises include determinations of nitrogen, organic matter, exchange capacity, exchangeable bases, pH, available phosphorus and potassium, nitrates in plant tissues, lime requirement of soils, neutralizing power of limestone, and sieve analysis of crushed stone. The procedures are carefully outlined, and drawings of the necessary apparatus are shown. The appendix contains a calculation of percentage error, acid-base titration curves, directions for preparation of reagents, and suggestions with respect to collecting, analyzing, and interpreting analyses of samples of farmers' soils. It is of interest to note that limestone quality is measured in terms of purity and percentages that pass the 8-mesh and 50-mesh screens.

Land for Tomorrow. By L. DUDLEY STAMP. Indiana University Press, Bloomington, 1952. Pp. 230, figs. 31. Price \$4.

The subtitle of this book is "the underdeveloped world." The primary aim of the author is to examine into our land resources, which total more than 33 billion acres, of which between 3 and 4 billion are under cultivation. On this land an estimated 28 billion bushels of cereal grains are being grown annually to feed a population approaching $2\frac{1}{2}$ billion. Special attention is given to the

possibilities of food production in the equatorial regions, well described by the phrase "regions of lasting difficulty." The evidence suggests that such land is not likely to be developed except where the soils are of recent volcanic origin. The author decides that there are "at least a couple of million square miles" of such land that, with difficulties that are enormous and are likely to remain so, might be brought under cultivation. This is a highly instructive book.

Moisture Requirements in Agriculture. By HARRY BURGESS ROE. McGraw-Hill Book Company, Inc., New York, 1950. Pp. 413, figs. 150. Price \$6.

As would be expected, the author of this book is concerned primarily with water problems as related to irrigation of arid lands, the total area of which for the United States is set at 21 million acres. For the earth as a whole, the acreage of irrigated land is estimated at 202 million acres. After a general discussion of soil-plant water relationships, the author considers soil water in terms of sources, disposition, flow, and measurement. Irrigation is dealt with in terms of principles and problems, time of application, water economy, methods, structures, pumping, and water requirements of specific crops. One chapter has to do with the general framework of irrigation farming and another with legislative and administrative features. The final chapter considers irrigation in humid climates, but it fails to measure up to the others in meeting the need for information in eastern United States. A lifetime of study and experience has gone into the writing of this book, and the results are quite apparent.

Our Garden Soils. By CHARLES E. KELLOGG. The Macmillan Company, New York, 1952. Pp. 232. Price \$4.

This book "is about garden soils, not gardening in general. It does not attempt to deal with matters that lie mainly in the field of horticulture, or landscape gardening, or insect and disease control, or engineering." So, it deals with what soil is, its profile, its organic matter, its water, and its reaction. One chapter has to do with balancing soil nutrients, and others are about lawns, starting and moving plants, and planning gardens. Soil preferences of a long list of garden plants are considered in detail. The book is interesting and constructive. It needs some good illustrations.

Modern Gardening. By P. P. PIRONE. Simon and Schuster, New York, 1952. Pp. 371. Price \$3.50.

The author of this book is responsible for the health of some 12,000 kinds of plants growing under glass and outdoors at the New York Botanical Gardens. The first part of the book deals with wonder drugs, planting fundamentals, foliage feeding, weed and insect killing, medicines for ailing plants, house plants, chemicals for the vegetable garden, and garden miracles. The wonder drugs are insecticides, fungicides, herbicides, and fertilizers. The garden miracles involve use of growth inhibitors, such as maleic hydrazide; permanent insecticides, such as octamethylpyrophosphoramidate; heredity-influencing agents, such as colchicine; seed-producing inhibitors, such as naphthaleneacetic acid; and agents to prevent fruit drop, such as potassium naphthaleneacetate. The second part is

devoted to answering 500 questions on a great variety of problems involved in growing horticultural and garden plants. This is an interesting and useful book.

Phosphorus Metabolism. Edited by WILLIAM D. McELROY AND BENTLEY GLASS. The Johns Hopkins Press, Baltimore, 1951. Pp. 762. Price \$10.

In the introduction to this symposium report, Otto Meyerhof comments on the point that this subject did not exist 25 years ago. Yet 51 persons presented papers and 25 others participated in the conference that was called to consider the various phases of the subject. The papers cover metabolism of polysaccharides, disaccharides, hexosephosphates, pentose, triose phosphates, and phosphorus-containing coenzymes, formation and use of active acetate, oxidative phosphorylation during electron transport, biochemistry of inorganic metaphosphates and pyrophosphates, chemistry and thermodynamics of phosphate bonds, and utilization of phosphate bond energy in biological systems. The work of some 125 scientists in this field is reviewed. An excellent summary of the present status of their work is given in a concluding chapter by Bentley Glass. This valuable book should have a place on the shelves of all soil-plant scientists.

The Reports of the Institute for Agricultural Research. Volume 1-2. Tohoku University, Sendai, Japan, 1950. Pp. 155, paper-bound.

This is Series D (agriculture) of the science reports of the research institutes of Tohoku University. It contains papers on phosphorus and iron absorption by rice, inoculation of rice plants with *Piricularia oryzae*, plant succession in natural grassland, tuberization in the potato plant, economic meaning of plant breeding, logic of rotation, double-crop farming technique for paddy fields, and seed-oyster production.

Soil Engineering. By MERLIN GRANT SPANGLER. International Textbook Company, Scranton, Pa., 1951. Pp. 458. Price \$6.50.

The first half of this introductory text on soils for students in engineering has all the earmarks of a text for agricultural students. It deals with the origin and nature of soil, its profile, structure, texture, density, and water relationships, and with methods of surveying and sampling. But the second half departs from the usual agricultural application to that of engineering, with chapters on frost action, stabilization, stress distribution, consolidation, shearing-resistance, slope stabilization, embankments, bearing-capacity, piles, and underground conduits. The book is well illustrated, mostly with excellent drawings, which delight the eye of the engineer and excite the envy of the agriculturist. Appended to each chapter is a list of questions and problems and a selected bibliography. This is an excellent text for engineers and merits study by those interested primarily in soil as related to agriculture.

A Study of Soils and Land Forms of the Chesapeake Bay Margins. By G. F. CARTER AND V. P. SOKOLOFF. Johns Hopkins University, Isaiah Bowman School of Geography, Baltimore, 1951. Pp. 37.

The study was sponsored by the Office of Naval Research. The authors used terraces of the Chesapeake Bay as time markers. They studied fields of known history, archaeological data, and distribution of trace elements. They applied the C14 technique. Supplemental surveys were made as far north as Canada and as far south as Florida. As a result, the hypothesis of a single process in the development of humid soils is presented. This permits of the conclusion that latasols are merely truncated podzols, resulting from erosion.

Surface Activity. By J. L. MOILLIET AND B. COLLIE. D. Van Nostrand Company, Inc., New York, 1951. Pp. 379. Price \$10.

The authors of this book divide the subject into physical chemistry, technical applications, and chemical constitution of synthetic surface-active agents. Among these agents are sulfonic acids and their salts, aliphatic sulfates, carboxylates, sulfinates, phosphates, amine salts, quaternary ammonium and pyridinium compounds, polyethenoxy compounds, derivatives of polyglycerols, and lignin sulfonic acids. Among the important uses considered are wetting-out and water-proofing processes, preparation of emulsions, dispersions of solids in liquid media, detergent processes, and a number of miscellaneous operations. References are given to the work of some 450 authors. About 100 trade names, with the composition of the products represented by them, are indexed. The material in the book is of great interest, both theoretical and practical.

Understanding Heredity. By RICHARD B. GOLDSCHMIDT. John Wiley & Sons, Inc., New York, 1952. Pp. 228, figs. 49. Price \$3.75.

In this introduction to the science of genetics the author deals with hereditary traits, fertilization, Mendelism, chromosomes, linkage, mutation, inheritance, collaboration of genes, multiple factors, multiple alleles, and some of the problems that lie ahead. He points out that man has a peculiar advantage because of his brain, which permits of passing on improvement by oral and written communication as well as by inheritance. He speaks of the use of Mendel's law in law cases involving questions of parentage. He philosophizes on what the Martians might do with the men on earth as captives in breeding for muscle and fat. He discusses the mapping of chromosomes, the terrible possibilities of atomic bomb explosions, and the relation of genetics to evolution. Appended is a long list of questions, a bibliography of books for supplemental reading, and a well-developed glossary. This is a highly interesting book.

Der Vegetationsversuch: I. Die Methodik der Wasserkultur höherer Pflanzen. By W. SCHROPP. Neumann Verlag, Radebeul und Berlin, 1951. Pp. 313, figs. 65. Price, D. M. 22.

This is the eighth volume of a series dealing with methods of research as applied to soils, fertilizers, feedstuffs, seeds, milk, and plants. It reviews the subject of water-culture techniques in detail, outlining the various methods that have been and are being employed, and giving the composition of the solutions used. The book is well illustrated and contains two plates in color. References are

given to the publications of some 500 authors. The author has made a highly important contribution to the literature on this subject.

World Population and Future Resources. Edited by PAUL K. HATT. American Book Company, New York, 1952. Pp. 262. Price \$3.50.

The proceedings of the second centennial academic conference of Northwestern University, held at Evanston, Illinois, in March, 1951, are recorded in this volume. The 20 speakers, specialists in their respective fields, dealt with population growth; land, water, mineral, fuel, and energy resources; food potentialities of the ocean; and technological advances in food production. One of the most penetrating presentations is that of Paul B. Sears on cultural factors in food production. He points out that "if our present knowledge could be applied ruthlessly and remorselessly, without any moral consideration except that of trimming population down to fit the earth and keeping it in balance, our problem is capable of solution." He reaches the decision that "better stewardship alone can only buy us time to face the ultimate problem of a rational adjustment between population and the resources which sustain it." The book comprises a valuable set of thought-provoking lectures.

THE EDITORS.

Serozems of Middle Asia. By A. N. ROZANOV. Academy of Sciences of the USSR, Moscow, 1951. Pp. 459, illus.

This monograph, in Russian, is another milestone on the road of Soviet literature on soil science. Together with Rode's earlier comprehensive treatise on "Podzolic Process" and Kovda's several volumes on saline soils, Rozanov's new book represents the growth of the series of fundamental monographs following the classical work of Dokuchaev on "Russian Chernozem."

Rozanov's monograph consists of seven chapters: 1. Geophysical characteristics of the serozem zone in Middle Asia; 2. "Hypergenic" processes (weathering) in the serozem zone; 3. Genetic types of the parent materials in the serozem zone; 4. Soils of the serozem zone; 5. Serozems as a genetic type of soils; 6. Principal features of the genesis and evolution of serozems; 7. Principal economic characteristics of serozems. A list of literature includes some 400 to 450 titles, of which hardly more than 10 per cent are references to non-Russian sources.

The region dealt with extends eastward from the Caspian Sea. Its northern boundary runs toward the southwestern shores of Lake Balkhash along the valley of the Chu River, that is, a little to the south of Lat. 45°N. It extends east to include the Ala-Kol depression. The southern boundary of the area runs from east to west along the 850-meter contour through the northern foothills of the Dzhungarski Alatau, Zailiiski Alatau, Kirgiz Range, and the western Tian-Shan and Pamir-Alai. Farther west the boundary bends to the southwest and extends into Afganistan and Iran. Thus, the region includes the southernmost part of Kazakhstan and most of the Uzbek and Tadzhik republics. Between the Caspian and Aral Seas it embraces the southern part of the Ust-Urt plateau. Almost three fourths of the entire region consists of fairly level lowland and

smooth plain having less than 1,000 feet of absolute elevation. Most of this area is occupied by sandy deserts and semideserts, including the Kara-Kum, Kizil-Kum, and Muyun-Kum.

The heart of the book is the longest, fourth chapter (pp. 156-328) and especially the section dealing with "systematics of soils of Central Asia" (pp. 173-318). The author points out that he does not attempt to present the genetic classification of these soils but merely gives a systematic description of various soils found in this part of the world. In his list, however, these soils are arranged into eight general groups or "types," which are subdivided into some 30 "subtypes." The subtypes are further broken down into "species," of which about 60 are mentioned in the list. Each species consists of "variants," which differ from one another in mechanical composition and range from heavy clays to sands and coarse stony soils. The principal "soil type" is defined as a broad group of soils that are developed under similar geophysical conditions and are similar to one another in the general trend of soil-forming processes as well as in general character of the profiles. The "subtypes" within a single type represent local or subregional modifications of the whole general unit, such as "central" (typical) and "northern" subunits. Species within a subtype or a type, if the latter is not divided into subtypes, are differentiated on the basis of relative degree of development (for example, weakly, moderately, and strongly developed).

Commenting on his list, the author points out that the serozem zone is occupied by many different soils, among which the "typical" serozems are not the most abundant. The greater part of the area is occupied not by typical serozems but by various geographically associated soils, such as takyrs, meadow soils, solonchaks, and solonized soils. Most of these associates bear some characteristics which show genetic relationships to the principal or typical serozem; in consequence, these soils might be described as serozemic.

The author presents descriptions of numerous individual soil profiles. In the reviewer's opinion, this part of the monograph is the least satisfactory. Soils are described in the most elementary, and in some cases even naive, terms. The whole long chapter runs as if it were written some 40 or 50 years ago. Expressions such as "somewhat darkish-brownish, rather moist" were not uncommon in the amateurish preliminary reports written at the very beginning of the century, but they sound anachronistic in 1951, and the reader begins to wonder whether any progress in the concepts and scientific analysis of the soil morphology has been made during the half of a century. Even such a cardinal subject as identification and designation of the genetic soil horizons appears to be almost meaningless. In most instances, horizons are not identified at all, and the data are referred just to so and so centimeters below the surface. Wherever the A, B, and C horizons are mentioned, the references are made to the horizons as defined by Dokuchaev and Sibirtzev, that is, horizons based on "relative content of humus" in the soil profile (footnote on p. 201). These concepts and definitions are more than 50 years old and certainly are out of date today.

Many pages are devoted to data obtained by chemical and mechanical analyses. The chemical data consist largely of not very informative analyses of conven-

tional water extracts, whereas mechanical analyses are much too fragmentary. In most tables only the content of a few mechanical fractions is reported. Complete mechanical analyses of the whole soil profile are very few.

Much more interesting and up to date are chapters 5 (pp. 329-408) and 6 (pp. 409-426), in which the author presents a fairly complete and well-done general picture of the serozem soil. This picture is summarized on pages 407 and 408. According to the summary, serozems are characterized by rather featureless profiles due to the weak differentiation of individual horizons, especially as regards the development of the textural profile. As a rule, the clay content of these soils is low because of the relatively low efficiency of chemical weathering. The clay that is present is usually in a state of stable microaggregation. The exchange capacity of serozems, naturally, is low, but the soils are completely saturated by the exchangeable bases. Of these, calcium and magnesium are the most abundant, comprising 85 to 95 per cent of the total. Soil solution usually has a weak alkaline reaction.

The carbonate content of serozems is typically high. A rather strong development of carbonate-enriched horizons is very common. A large part of the carbonates in the profile, however, consists of residual lime inherited from the unleached parent material. The humus content of serozems, on the other hand, is very low, and what is present is distributed throughout a horizon of considerable thickness. The humus in serozems consists largely (30 to 40 per cent) of proteinic substances. Hence, its carbon-nitrogen ratio is conspicuously narrow, ranging from less than 5 to about 7, as contrasted with 10 to 14 in the chernozems. Accumulation of humus in serozems is precluded by the complete mineralization of fresh organic residue within a year, which indicates a conspicuously high biochemical activity in these soils.

Most serozems have a rather friable consistence and fairly high porosity. Absence of "agronomic" crumb structure, but fairly good development of microaggregation, is typical. The content of all essential plant nutrients, with the exception of nitrogen but including the minor and trace elements, in serozems is high and compares favorably with the best agricultural soils, including the very best chernozems. The phosphorus content amounts to 0.15 to 0.20 per cent, most of which is in nonavailable form. Water-soluble phosphates are virtually absent; therefore application of superphosphate is hardly less effective than the application of nitrogenous fertilizers.

Rozanov's interpretation of probable genetic relationships between the various regional soils and of the general trend of evolution of the zonal serozem soil complex is based largely on scholastic and highly controversial doctrines of the late V. R. Williams. It contains some interesting and stimulating ideas but lacks objective documentation and, hence, is unconvincing.

Despite its several largely technical shortcomings, the book as a whole is a very valuable contribution to soil science and provides abundant first-hand information about one of the least known and least understood groups of zonal soils. By the resolution of the Academy of Sciences of the USSR, its author was awarded the Dokuchaev premium.

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SOIL SCIENCE

VOLUME 74

September 1952

NUMBER 3

STANDARD FERTILIZATION AND LIMING AS FACTORS IN MAINTAINING SOIL PRODUCTIVITY

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Received for publication December 11, 1951

In more or less humid regions where acid soils are predominant, liming is generally recommended as an indispensable to soil fertility. The bases for this recommendation have been results obtained in liming trials on acid soils. On unlimed plots only poor yields have been obtained; after adequate liming, yields have been satisfactory.

The writer has worked out a method of computing the amounts of plant nutrients that should be added to a given soil to produce maximal crop yields insofar as a lack of plant nutrients is the limiting factor of production. This method of fertilization has been called *standard fertilization* because it is supposed to bring about a suitable nutritional standard in the soil. When standard fertilization has been tested in liming trials on acid soils it has produced such heavy yields on unlimed plots that addition of lime has resulted in only small, if any, increases. Liming has become superfluous and unprofitable.

HISTORICAL

Early experience of the writer (13) indicated that very good yields of red clover, for instance, could be obtained on well-managed soils that had not been limed since they were brought under cultivation centuries ago and that were found to be acid to litmus. Addition of lime gave no increases.

Many years later the problem was attacked scientifically. During the excursion following the First International Congress of Soil Science, the idea was conceived that neutral or even alkaline soils could be formed by "acid" rocks, and subsequently it was found that finely ground granite and gneiss, commonly described as acid rocks, induced a pronounced alkaline reaction in an aqueous suspension. Leaching produced an acid reaction (3). The all-important role of leaching in soil reaction was thus demonstrated.

The low productivity of acid soils has generally been attributed to the injurious action of H ions. Good yields had been recorded however, on well-managed acid soils to which farmyard manure and chemical fertilizers had been applied. Thus a good supply of nutrients in the soil appeared to moderate or wholly offset the supposedly injurious action of H ions. The *concentration* of the soil solution appeared to be important. Common nutrient solutions were found to be very acid. Nevertheless, good yields were obtained.

In an experiment barley was found to grow as well in a nutrient solution of common concentration at pH 3.75 as at pH 6.75. When the solutions were diluted, the yields decreased much more rapidly in the acid than in the neutral solution (4). Thus a certain relation was found to exist between crop production on acid soils and in acid solutions. In a concentrated acid solution and in a well-fertilized acid soil, the yields are good, whereas in diluted acid

solutions and in nonfertilized acid soils the yields are poor. The amount of nutrients present, and not the reaction, determined crop production.

In subsequent experiments it was found that Ca ions exhibited a striking antagonism to H ions, when barley was grown in acid solutions (6). Still earlier in 1924, Lundegårdh (22a) had demonstrated antagonism between Ca ions and H ions during germination and growth of wheat.

The idea was then conceived that the difference between an acid soil and a neutral or a slightly alkaline soil lies not in acidity, or H-ion concentration of the soil solution, but in nutrients available to the plant. The first attempt to determine the amounts of readily available nutrients in mineral soils of arable land gave striking results. Neutral or slightly alkaline soils were found to be rich in readily soluble plant nutrients; but with increasing acidity, a marked decrease was noted in such nutrients. Distinctly acid soils were found to

TABLE 1
Amounts of readily soluble plant nutrients in typical Swedish arable soils
In mgm. per kgm. soil

TYPE OF CLIMATE	SOIL LAYERS	SOIL TYPES	pH	READILY SOLUBLE				
				P	K	Ca	Mg	Mn
Dry	cm.							
	0-20	Medium clay	7.1	46	86	2,111	428	11
	100	Medium clay	8.3	76	208	28,940	5,711	79
Wet	0-20	Medium clay	5.7	1.2	41	779	256	12
	100	Heavy clay	7.7	71	73	8,840	1,880	187

TABLE 2
Amounts of readily soluble plant nutrients in the topsoil of arable land in two districts of Sweden
In kgm. per hectare

TYPE OF CLIMATE	NUMBER OF ANALYSES	SOIL TYPES	pH	P	K	Ca
Dry	30	Heavy clay	7.9	248	503	20,150
Wet	50	Light clay	5.6	9	75	2,160

be very poor in readily soluble plant nutrients (7). A close relationship of humidity of climate, soil reaction, and soil fertility was proved. In regions with such a dry climate that podzolization does not occur, the soils are neutral or slightly alkaline in reaction and more or less rich in readily soluble plant nutrients; in short, they are fertile soils. Conversely, in regions with a wet climate, the soils are podzolized and the readily soluble plant nutrients are lost by leaching. The result is an acid soil poor in plant nutrients, an infertile soil.

The relation of humidity of climate, soil reaction, and amount of readily soluble plant nutrients is clearly brought out in table 1.

In the dry climate (precipitation about 500 mm. annually) the podzolization has been slight. The soil reaction in the topsoil is still neutral. The amounts of readily soluble plant nutrients are comparatively high: it is a fertile soil. At a depth of 100 cm. the content of nutrients, especially of Ca, is still higher.

In the wet climate (annual precipitation about 1,000 mm.) the soil has evidently been podzolized. The soil reaction is acid, and the amounts of readily soluble plant nutrients are reduced. Available phosphorus has almost disappeared, and the only quantity of readily

soluble calcium is comparatively high. It is an infertile soil, but it would seem reasonable that any attempt to increase the fertility should aim primarily at an increase in phosphorus content rather than calcium. At a depth of 100 cm. the soil is comparatively rich in readily soluble plant nutrients.

In table 2 the influence of climate upon the content of P, K, and Ca is still more obvious.

The next question was: Are low yields in acid soils caused by the acid reaction, by the insufficient content of plant nutrients, or by both these factors in combination? The first attempt to answer this question was made in pot culture experiments. Samples of soils were collected from many parts of the country: neutral or slightly alkaline soils from regions with a low or moderate precipitation, and acid soils from wet regions. The contents of readily soluble plant nutrients were determined, and a neutral soil known to be very fertile was chosen as the standard soil. This soil was fairly rich in plant nutrients. In the acid soils there was a gradual decrease in plant nutrients with increasing acidity. To the acid soils were added such amounts of plant nutrients as to make each one equal to the nutritional standard of the neutral soil. An attempt was made to provide *standard fertilization* without change in the soil reaction. In addition to the standard fertilization series, a completely

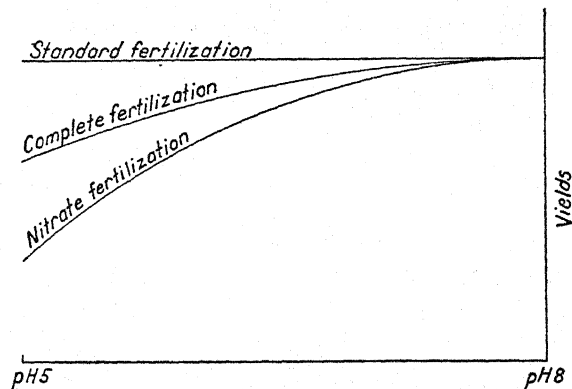


FIG. 1. INFLUENCE OF SOIL REACTION AND FERTILIZATION ON YIELDS OF BARLEY

fertilized series and a nitrate-fertilized series were set up. Golden barley was grown. Standard fertilization gave equal yields in mineral soils between pH 8 and pH 5 (fig. 1). With complete fertilization, yields fell off with increasing acidity. This tendency was still more pronounced in the nitrate series. Evidently the limiting factor of crop production was not soil reaction but the amounts of available nutrients. The innate nutrient contents of the neutral or slightly alkaline soils were sufficient to bring about maximal yields, but those of the acid soils were inadequate. Complete fertilization increased the yields considerably, and standard fertilization induced equality with the neutral soils (7).

MATERIALS AND METHODS

To test standard fertilization under field conditions experiments were laid out in various parts of the country characterized by different degrees of humidity. The experimental fields were selected under growing crops to ensure uniform areas (9). The weed flora was also used as an indicator of uniformity. Within the piece of land tentatively chosen for the experiment, several samples of topsoil and of subsoil were collected, and a profile was dug to a depth of

100 cm. for samples of deeper layers. The samples were analyzed for readily soluble plant nutrients by the following method:

Ten grams of mineral soil (less of humus soil) plus 75 ml. H_2O was titrated with a mixture of 90 gm. of lactic acid (sp. gr. 1.21) plus 10 gm. of concentrated HCl diluted to 1,000 ml., until well below pH 3.5. The sample was occasionally shaken and left overnight, after which the reaction was again determined. It was then generally above pH 3.5, but the amount of acid necessary to change the reaction to near pH 3.5 could be computed. One hundred grams of soil (less of humus soil) was then shaken for 18 hours with the amount of acid found to be sufficient to give an ultimate pH of 3.5, the volume of the extraction solution being 800 ml. After extraction, the pH was measured, and any sample outside pH 3.4-3.6 was discarded. The Si, P, K, Ca, Mg, Na, and Mn contents of the extract were determined. Humus content was determined by Balks' (17) wet-combustion method, total nitrogen by the common Kjeldahl method, and lime-absorbing capacity by Jensen's method (21). On the basis of the analytical data were computed the amounts of fertilizers needed, in addition to available farmyard manure, to bring about standard fertilization.

The whole experimental field received standard fertilization, and it was thereafter divided into plots that were unlimed and limed to 1/32, 1/16, 1/8, 1/4, 1/2, and 1/1 of the lime-absorbing capacity of the soil. The quantity 1/1 denotes the amount of lime necessary to bring the topsoil layer to pH 7.0. The plots were run in series of four. On each experimental field the common rotation of the farm was followed. The yields were recorded during one rotation period, generally for 6 years in succession. Samples of the crops were taken for analysis, and in several cases the entire yields were collected as feed for experimental animals—rats, guinea pigs and rabbits. In all, more than 50 experimental fields were laid out and harvested (12).

RESULTS

Mineral Soils

Experimental field K₅₁ was on the Stora Löfhulta estate, Eskilstuna, on the southern shore of Lake Mälaren about 60 km. west of Stockholm. The climate of the region is fairly dry, the annual precipitation being about 600 mm. The soils are mostly sedimentary clays, glacial and postglacial. The soil of the experimental field was a heavy postglacial clay. The clay content (<0.002 mm.) of the topsoil layer was 51.3 per cent and that of the subsoil 60.0 per cent. The amounts of readily soluble plant nutrients in the soil are recorded in table 3.

Standard fertilization for the entire rotation period, six crops, was calculated at 45 tons farmyard manure (the usual application on the estate) and 72 kgm. P per hectare. No N or K was applied.

The rotation was as follows: 1, fallow (start of experiment); 2, winter wheat; 3, spring wheat; 4, hay; 5, hay; 6, spring wheat; 7, oats. The hay crops were a mixture of red clover and timothy grass.

Yields of winter wheat and combined average yields from the experimental field are recorded in table 4. The yields were uniformly high between pH 5.5 and pH 7.1.

Experimental field K₁₀₃ was on the Vapnö estate, Halmstad, on the west coast

of Sweden. The climate of the region is comparatively wet, the average annual precipitation being about 800 mm. The soils are sedimentary glacial clays. The soil of the experimental field was a medium clay with 35.2 per cent clay particles in the topsoil layer. The amounts of readily soluble plant nutrients, determined in the upper 20-cm. layer only, were as follows, in milligrams per kilogram of air-dry soil: Si, 60; P, 3.7; Ca, 1,257; K, 20; Na, 41; Mg, 757; Mn, 15. The topsoil had a pH of 5.7, humus content 4.10 per cent, total nitrogen 0.201 per cent, lime-absorbing capacity 30 tons of slaked lime per hectare, volume weight 1.11.

TABLE 3

*Amounts of readily soluble plant nutrients in the soil of experimental field K₅₁**
In mgm. per kgm. air-dry soil

SOIL LAYERS	pH	Si	P	Ca	K	Na	Mg	Mn
Topsoil, 0-20 cm.	5.5	33	5.5	1,218	35	123	360	9
Subsoil, 20-40 cm.	5.9	177	1.8	1,000	25	92	240	14

* Topsoil: humus content 7.30 per cent, total nitrogen 0.377 per cent, lime-absorbing capacity 16.5 tons of slaked lime per hectare, volume weight 1.23.

TABLE 4

Yields of winter wheat and average yearly yields in harvest units on experimental field K₅₁
On per-hectare basis

LIMING		pH	1ST YEAR WINTER WHEAT	1ST-6TH YEARS HARVEST UNITS*	
Degree	Amount			Number	Difference
	kgm.		kgm.		
0	0	5.5	5,900	4,100	—
1/32	516	5.6	5,900	4,020	-80
1/16	1,032	5.8	5,820	4,090	-10
1/8	2,063	6.0	5,840	4,110	+10
1/4	4,125	6.4	5,780	3,990	-110
1/2	8,250	6.8	5,880	3,980	-120
1/1	16,500	7.1	6,200	4,150	+50

* One harvest unit is equal to feeding value of 1 kgm. barley grain. A harvest of 6000 kgm. of grain per hectare corresponds to 90 bushels per acre.

Standard fertilization for the first 4 years of the experiment was calculated at 35 tons of farmyard manure (normal supply), 100 kgm. N, 48 kgm. P, and 33 kgm. K per hectare.

The rotation was as follows: 1, sugar beet (when the experiment was begun); 2, spring wheat; 3, hay; 4, hay; 5, mixed grain; 6, oats and vetches cut as green fodder; 7, winter wheat. Yields of only the first three crops were recorded (table 5). The yields of sugar beet were not especially high, perhaps because the experimental field was at the northern limit of the beet-growing area, but they were not influenced by liming or by soil reaction. The "straight line" for standard fertilization, as brought out in figure 1, was attained.

Humus Soils

Experimental field K₇₈ was on Bråtagärde farm in the hills about 20 km. inland from the west coast. The climate of the region is the wettest recorded among farming districts in Sweden, the annual precipitation often exceeding 1,000 mm. The experimental field was on a peat soil brought under cultivation a few years earlier. The peat was composed for the most part of poorly humified *Sphagnum* sp. The amounts of readily soluble plant nutrients are recorded in table 6.

TABLE 5

Yields of sugar beet and average yearly yields in harvest units on experimental field K₁₀₈
On per-hectare basis

LIMING		pH	1ST YEAR, SUGAR BEET	1ST-3RD YEARS HARVEST UNITS*	
Degree	Amount			Number	Difference
	kgm.		kgm.		
0	0	5.7	33,090	4,540	—
1/32	936	5.8	33,090	4,340	-200
1/16	1,875	5.9	33,390	4,370	-170
1/8	3,750	6.1	31,250	4,250	-290
1/4	7,500	6.4	34,280	4,470	-70
1/2	15,000	6.6	31,910	4,330	-210
1/1	30,000	6.8	32,370	4,500	-40

* One harvest unit is equal to feeding value of 1 kgm. barley grain.

TABLE 6

*Amounts of readily soluble plant nutrients in the soil of experimental field K₇₈**
In mgm. per kgm. air-dry soil

SOIL LAYER	pH	Si	P	Ca	K	Na	Mg	Mn
Topsoil, 0-20 cm.	4.3	47	9.2	2,060	45	154	1,205	22
Subsoil, 20-40 cm.	4.3	56	15.8	1,040	65	185	284	9

* Topsoil: humus content 64.0 per cent, total nitrogen 0.977 per cent, lime-absorbing capacity 30.2 tons of slaked lime per hectare, volume weight 0.53.

Standard fertilization for a 6-year rotation was computed at 45 tons farmyard manure (normal supply), 74 kgm. P, and 66 kgm. K per hectare. No N was necessary.

The rotation was planned as follows: 1, winter rye; 2, hay; 3, hay; 4, hay; 5, oats; 6, oats. Actually the following crops were harvested: 1, winter rye; 2, none, because the crop was killed in the winter; 3, oats; 4, hay; 5, hay; 6, hay.

The yields are recorded in table 7. The average yields are very high in view of the exceedingly poor type of soil. The hay crop of the second year is also extremely good, and more than 60 per cent of red clover in the hay at pH 4.3 is significant. It is clear that suitable fertilization can make very poor soils highly productive, and red clover—commonly said to require an almost neutral

soil reaction—may grow luxuriantly in very acid soil, provided the nutritional standard is satisfactory.

A special type of organogenic soils, gyttja, commonly contain large quantities of H_2SO_4 in dry regions. They are very acid, partly on account of the H_2SO_4 , and are unproductive. The writer (5) found an acidity caused by mineral acids to be injurious to barley but not an acidity caused by "humic acids," that is, aqueous extracts of poorly humified sphagnum peat. The gyttja soils were brought to maximum fertility by standard fertilization without liming in some cases, but not in others. For that reason, these soils are excluded from the present discussion.

TABLE 7
Yields of hay and average yearly yields in harvest units on experimental field K₇₈
On per-hectare basis

LIMING		pH	5TH YEAR, HAY		1ST-6TH YEARS HARVEST UNITS*	
Degree	Amount		Total amount	Red clover	Number	Difference
	<i>kgm.</i>		<i>kgm.</i>	<i>per cent</i>		
0	0	4.3	13,950	62.5	4,640	—
1/32	944	4.4	13,650	62.6	4,620	-20
1/16	1,888	4.6	13,300	66.2	4,580	-60
1/8	3,775	5.0	13,670	64.5	4,650	+10
1/4	7,550	5.4	13,850	60.0	4,520	-120
1/2	15,100	5.8	13,740	65.0	4,640	0
1/1	30,200	6.4	13,270	65.8	4,520	-120

* One harvest unit is equal to feeding value of 1 kgm. barley grain.

DISCUSSION

Soil Reaction and Crop Production

Some crop plants, for instance, wheat, barley, red clover, and sugar beet, are said to give optimum yields only in neutral or slightly alkaline soils. On the other hand, oats, rye, timothy grass, and potatoes, are reported to prefer acid soils (2). The results recorded in this paper make it clear that high yields of wheat, red clover, and sugar beet have been obtained at low pH values. In other cases it has been shown that oats, rye, and other presumably acid-loving plants have given maximum yields at high pH values.

The dominant factors of plant production in this respect are the availability of plant nutrients in the soil and the ability of various plants to utilize the nutrients, in other words, the feeding power of plants. The following explanation may be given: Plants reported to need a neutral soil have a low feeding power. They thrive only on soils comparatively rich in readily soluble plant nutrients. On the other hand, plants found to grow well on acid soils have a high feeding power. They are able to utilize the small quantities of readily soluble plant nutrients present in such soils. For both groups of plants, available nutrients and not soil reaction is the decisive factor.

Golden barley, reported to thrive only at pH 7 to 8, and golden rain oats,

said to prefer pH 5 to 6 (2), were grown in pot cultures in an acid soil at pH 5.4 and in a slightly alkaline soil at pH 7.6. Standard, complete, nitrate, and no fertilization formed the series included in the experiment. Barley gave good results in acid soils only when sufficient amounts of nutrients were added. Oats grew better than barley in both soils. Barley often absorbed larger quantities of nutrients than oats in the fertilized series, but the reverse was true in the unfertilized series. The results indicate that barley prefers neutral or slightly alkaline soils because of the greater supply of nutrients in such soils, whereas oats, on account of their high feeding capacity, are able to grow in acid soils which are generally poor in readily available nutrients (8).

In another investigation, farmers collected and handed in soil samples from fields of good, medium, and low yields of sugar beet. It was found that amounts of readily soluble plant nutrients and not soil reaction was the dominant factor (16). In most cases it is unnecessary to lime arable soils to change the reaction. Albrecht (1) pointed out that liming should not be used in fighting soil acidity.

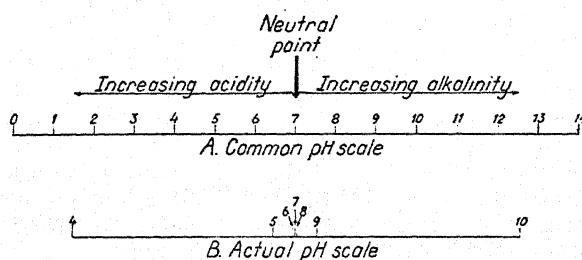


FIG. 2. COMMON pH SCALE COMPARED WITH ACTUAL pH SCALE

The common scale exaggerates the small variation in H-ion concentration between pH 5 and 8.

Wild plants seem to conform to the same rule. Sheep sorrel (*Rumex acetosella*) has been said to indicate lime deficiency, or an acid soil reaction, but it was found to grow on all kinds of soil from very poor and acid raw humus to very rich neutral soils. In pot cultures, it gave equal yields between pH 4.9 and 7.3. The species was found to possess a high feeding capacity. It is able to grow well on soils poor in nutrients, but it grows still better on rich soils. The limiting factor for its occurrence was found to be the need for good illumination during the seedling stage, which is of unusually long duration. Only in sparse vegetation on poor soils are the seedlings normally able to survive. On rich soils sheep sorrel occurs only when other, fast-growing plants are held back by unfavorable circumstances (11).

Analyses of soil samples collected in various plant habitats on Mt. Kinnekulle indicate that amounts of readily soluble phosphorus are an influential factor in plant distribution. The following dominance was noted: at a low phosphorous content, spruce (*Picea Abies*); at a somewhat higher phosphorus content, birch (*Betula verrucosa*); whereas oak (*Quercus robur*), ash (*Fraxinus excelsior*) lime

tree (*Tilia cordata*), cherry (*Prunus* sp.), and beech (*Fagus sylvatica*) seemed to thrive only on soils comparatively rich in phosphorus (16).

Yields of crop plants and distribution of plants in nature thus seem to be influenced by amounts of plant nutrients in the soil far more than by soil reaction.

The absence of any influence of soil reaction upon crop yields—at least when standard fertilization is used—as demonstrated in tables 4, 5, and 7, may be explained by the graphs in figure 2. The pH scale usually is illustrated as in figure 2A, which greatly exaggerates the changes in H-ion concentration around pH 7. The pH scale is logarithmic and is very difficult to illustrate. But in figure 2B, a small portion is drawn. It shows that the increase in H-ion concentration is comparatively small between pH 8 and 5, the range which the author has found to exist in mineral soils studied. That such a small increase in acidity can be counteracted by suitable fertilization does not appear unreasonable. In humus soils an acid reaction of pH 4 may be encountered, but table 7 shows that even such an acid reaction is without influence upon crop yields when standard fertilization is used.

Lime Content of Soils

It is a common concept that acid soils are deficient in lime, but the analytical data make it clear that the Ca content is comparatively high even in such soils. The content of readily soluble Ca is seldom less than a hundred times that of readily soluble P and, generally, it is several hundred times greater. The uptake of Ca by plants is of about the same magnitude as that of P. Furthermore, Ca is usually added to a soil in farmyard manure and artificial fertilizers in greater quantities than the need of the crops (figure 5). It seems safe to assume, therefore, that the Ca content is seldom, if ever, the limiting nutrient factor of crop production on acid soils. The question is, then, whether Ca plays any other important role in the soil.

It seems to be commonly accepted that a high Ca content is necessary in a clay soil to maintain proper structure. Consequently, liming is recommended on heavy soils. Keen (22) has emphasized, however, that large amounts of lime are needed for measurable reduction of the soil resistance against an implement. In the writer's investigation no appreciable effect of liming upon soil structure could be noted. Tables 4 and 5 summarize the yields on clay soils, and in table 4 at least we are dealing with a heavy clay. But liming, even in amounts never met with in normal farming, has had no influence on the yields. This must mean either that lime has had no influence on soil structure or that an improvement of soil structure has no influence on crop yields. The latter assumption is absurd. Hence, we must accept the fact that liming has exerted no measurable influence on soil structure under the conditions of the investigation. The fact that the soils are generally frozen during at least part of the winter may have been of decisive influence.

At Lanna Experimental Station liming at a rate of 6,000 kgm. CaO per hectare on a medium clay has been found to increase the tendency to winterkilling of

wheat when there is no snow cover (15). The explanation offered is that the limed soil will absorb more water in the uppermost layer—a structural change. The repeated freezing and thawing of the soil lift the plants until the roots snap.

Action of Lime in Soil

In many cases liming has been demonstrated to increase crop production. Thus, liming must, under some circumstances, enhance soil fertility.

When liming on acid soils increases crop yields, the cause cannot primarily be the change in soil reaction, for tables 4, 5, and 6 show that the yields were unaffected by varying soil reaction. Liming must in some way influence the nutritional conditions of the soil.

Action on organic matter. When lime is added to a soil it will start a more or less rapid decomposition of the organic matter. The ultimate result is an increased nitrate production, which is often noted in the appearance of crops, especially of grain crops, in which lodging may occur (12). In many cases the quantity of nitrate available is the limiting factor of crop production; hence liming tends to increase the yields. Mattson (23) has found β -humus formed by autoxidation on a heavily limed acid soil.

Action on phosphates. Under conditions reported to represent or resemble those of acid soils, Gaarder (19) found phosphoric acid insoluble or nearly so under moderately acid conditions. A correlation was thus found to exist between low yields on acid soils and the insolubility of soil phosphates. As the writer (7) has pointed out, however, high yields have in many cases been recorded on acid soils, especially on humus soils, and in those cases phosphorus must have been available. Presumably, humus makes soil phosphates available in acid soils. Later, Gaarder and Grahl-Nielsen (20) ascertained the influence of humus extracts on the solubility of phosphates. They found the reaction between pH 2 and 8 in presence of humus extracts to be without influence on the solubility of phosphates. By mixing phosphates with humus-forming material, especially farmyard manure, the writer (10, 12, 14) has been able to overcome the influence of soil reaction on the solubility of added phosphate fertilizers. The influence on the crop yields is demonstrated in tables 4, 5, and 7.

Liming will affect the availability of soil phosphates in still another way. In pot experiments (7, 8) in which no phosphates were added it was found that the uptake of soil phosphorus by the plants was considerably increased when nitrates were given. A suitable supply of nitrates will increase the feeding capacity of the plants. Liming tends to increase the nitrate production in the soil and will in that way also increase the uptake of soil phosphorus. Mattson *et al.* (25) found a relationship between inorganic P and β -humus in a heavily limed acid soil. An increase in inorganic P is accompanied by a decrease in β -humus. The obvious conclusion seems to be that the β -humus displaces the phosphate ions and pushes them deeper into the profile.

Action on potash. An increase of the Ca-ion concentration in a soil by liming must tend, through ion exchange, to increase the K-ion concentration in the soil

solution. Where available potash is the limiting factor of crop production, liming must tend to increase the yields, at least of the first crop.

Action on minor elements. Mattson *et al.* (24) have studied especially the effect of liming on the forms and availability of manganese. Recently Troug (28) summarized our present knowledge in this field. Generally, liming up to neutrality has been found to diminish the availability of many of the minor elements.

Liming tends to decompose soil organic matter and to increase the utilization of the supply of major nutrients in soil. Mattson *et al.* (26) believe that the organic matter is the chief source of P, as well of the N, made available when a soil is limed. Liming will thus act as a more or less short-lived stimulant.

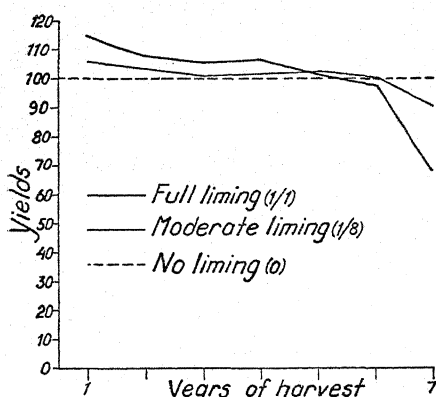


FIG. 3

FIG. 3. INFLUENCE OF LIMING ON YIELDS FOR 7 SUCCESSIVE YEARS

Average yields, expressed as harvest units, from 13 experimental fields on mineral soils with pH values between 5.2 and 5.6, standard fertilized.

FIG. 4. CORRELATION BETWEEN READILY SOLUBLE PLANT NUTRIENTS AND SOIL FERTILITY

A. Soil extraction by identical solutions. B. Extraction at identical H-ion concentration by writer's method.

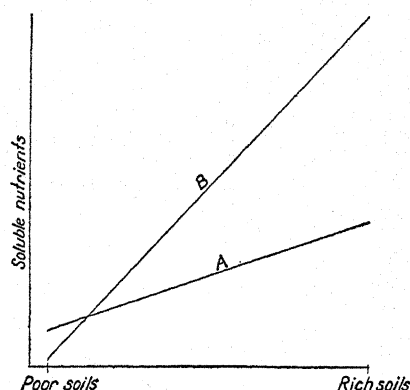


FIG. 4

Especially in German text books of the 18th century, liming is claimed to cause "prosperous parents but poor children," a statement which Thaer (27) tried to contradict.

That liming acts as a stimulant of comparatively short duration is shown in figure 3. The graphs (12) indicate that the action of lime was greatest in the first year and gradually diminished. At the end of a rotation of 6 to 7 years' duration, the yields of a limed soil may drop considerably below those of an unlimed soil.

Standard Fertilization

Standard fertilization is intended to produce optimum nutritional conditions in the soil. In addition to the amounts of nutrients already existing in a soil, sufficient quantities of fertilizers and preferably also of farmyard manure are

added to make up the balance. The foundation of standard fertilization is the method of soil analysis outlined under "Materials and Methods." The soil extraction is always made at the same H-ion concentration, at pH 3.5, which has been found to give reliable results. Figure 4 illustrates the general trend when soils are extracted with one solution identical for all soils and when the extraction is made according to the writer's method. Obviously, the latter method brings out the difference in fertility more distinctly than does the former, and plant experiments have corroborated this.

The calculation of the need for fertilization must be based not only on the results of a dependable soil analysis but also on a study of the soil *in situ*. The person who proposes to calculate standard fertilization must himself collect the soil samples. It will then be possible to study all the factors, besides plant nutrients in the soil, that make up the crop-producing power, in particular, and

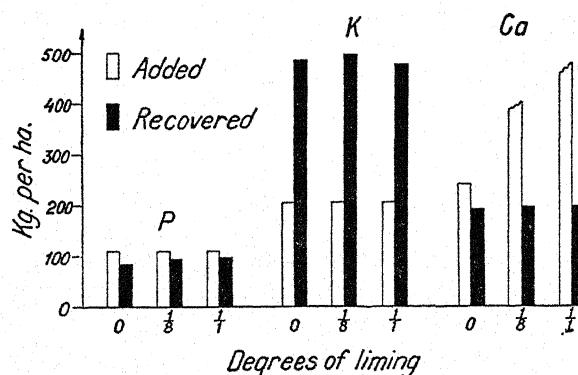


FIG. 5. QUANTITIES OF PLANT NUTRIENTS ADDED TO SOIL AND QUANTITIES RECOVERED IN CROPS UNDER INFLUENCE OF STANDARD FERTILIZATION AND DIFFERENT DEGREES OF LIMING

to estimate the optimum yields when the nutritional conditions are made optimal by standard fertilization.

Under optimum nutritional conditions in the soil, various crop plants contain somewhat constant percentages of plant nutrients. The need of nutrients, in kilograms per hectare, for the production of a certain yield can be computed with a satisfactory degree of accuracy. To what extent the innate soil nutrients can participate in the support of the crops to be grown must be judged from the results of the analysis and from the soil type. Finally, the fertilizers used must be chosen according to their suitability. For instance, on very acid humus soils, especially on gyttja soils containing H_2SO_4 , phosphorus should be given as basic slag; all phosphate is mixed with farmyard manure or other humus-forming material (14). Sulfate of ammonia must be restricted to calcareous soils. Brenchley (18) has pointed out that use of $(NH_4)_2SO_4$ caused lime deficiency, but where no $(NH_4)_2SO_4$ had been used, liming was found to be unnecessary or even harmful. On a visit to England during the summer of 1951, the writer considered it obvious that prolonged use there of $(NH_4)_2SO_4$ has been harmful,

especially on light, poorly buffered soils. Incidentally, liming is held in high esteem.

Figure 5 shows graphically the calculated necessary additions of nutrients to a soil and the quantities recovered in the crops during a 6-year rotation. The graphs represent the results obtained on experimental field K₅₁. More P was added than was subsequently recovered in the crops. Utilization of the added P must, however, be considered very good. Much more K was found in the crops than was added to the soil. The K of the soil was utilized to a great extent. Even on unlimed plots, more Ca was added in farmyard manure and superphosphate than was taken up by the crops.

Soil reaction and liming exerted virtually no influence on the utilization of the nutrients by the crops. Only in the case of P has liming increased the uptake to any measurable degree. Since very high yields were obtained on field K₅₁, the nutritional conditions shown in figure 5 must have been favorable for the crop plants. Thus it appears possible to calculate a suitable fertilization on the basis of the soil analysis used.

The calculation of standard fertilization is, at present, a combination of the art of judging various factors and the science of soil analysis. The results have been satisfactory, as demonstrated in tables 4, 5, and 7. If standard fertilization is to be commonly used, the art of judging the concurrent factors must be reduced to a minimum by reliable analytical methods. This would require very comprehensive investigations.

SUMMARY

In more or less humid regions the soils become podzolized, which causes an acid reaction and a low content of readily soluble plant nutrients, especially of phosphorus. The content of readily soluble calcium was found to be a hundred or several hundred times higher than that of readily soluble phosphorus. It is a lack of plant nutrients and not an acid reaction that makes an acid soil unproductive. The calcium content has never been found to be the limiting factor.

Standard fertilization is intended to bring about optimum nutritional conditions in the soil. The amounts of nutrients needed for that purpose are computed on the basis of the results of a reliable soil analysis. Comparatively small amounts of fertilizers have been found necessary.

When acid soils, mineral soils between pH 8.0 and 5.0, and humus soils down to pH 4.0 were standard fertilized, the yields were very high and were unaffected by soil reaction.

Liming of standard fertilized soils produced no profitable increase in yields, probably because standard fertilization alone had produced maximum yields under prevailing conditions.

Standard fertilization seems to induce lasting fertility in a soil, whereas liming produces a stimulation of shorter duration. The predominant action of lime in the soil seems to be an accelerated decomposition of organic matter, which will result in increased nitrate production.

Standard fertilization has increased yields considerably on previously infertile

soils. For that reason it must be of considerable interest in areas where the supply of plant nutrients in the soil is the limiting factor of crop production.

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RELATION OF COLLOIDAL HYDROUS OXIDES TO THE HIGH CATION-EXCHANGE CAPACITY OF SOME TROPICAL SOILS OF THE COOK ISLANDS

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Received for publication October 9, 1951

A number of lateritic soils collected by L. I. Grange and J. P. Fox during a soil survey of islands of the Lower Cook Group have high cation-exchange capacities. The organic carbon contents, particularly of the subsoils, are not enough to account for these high figures.

High capacities of tropical soils have been noted by other workers including Tanada (7) and Kelley and Page (4), who have investigated Hawaiian soils. Tanada used exchange capacity as a factor in grouping his soils but did not draw any conclusions regarding the cause of high values. Kelley and Page reported that the cation-exchange properties of such soils were related to amorphous material. It is significant, however, that Kelley (5) in 1948 relegated amorphous material to a very minor role with the conclusion that "cation exchange in soils is not primarily due to amorphous substances."

Preliminary x-ray examination of the soils of the Cook Group showed that crystalline gibbsite, boehmite, goethite, anatase, and in some cases kaolin were present. The amount of crystalline material indicated by x-ray diffraction seemed insufficient, however, to account for all of the inorganic matter. No crystalline clay minerals such as montmorillonite, vermiculite, or illite which could have caused high exchange capacities were present.

Fusion analyses showed that these soils contained considerable amounts of alumina, iron oxide, and titanium oxide, and all had low silica contents. The small amounts of silica could be accounted for by the kaolin contents.

The oxides of aluminum, iron, and titanium appeared to be the only possible sources of exchange capacity, and since crystalline forms of these oxides have low capacities it seemed that amorphous oxides should be considered.

Differential thermal curves of the soils and clays had multiple endothermic peaks, some of which were due to the crystalline substances identified by x-rays. Other peaks, however, differed from those usually obtained from soils. The nature of the endothermic reactions causing the unusual peaks was consistent with the possibility that they were due to the loss of held water or hydroxyl from hydrous oxides.

Colloidal hydrous oxides of aluminum, iron, and titanium prepared in the

¹ The writers thank Dr. L. I. Grange for suggestions and encouragement, F. T. Seelye of Dominion Laboratory, Department of Scientific and Industrial Research, for most of the silicate analyses, and K. I. Williamson of Dominion Physical Laboratory, for electron micrographs. Thanks are due also to A. Valk, J. A. Robertson, and G. G. Claridge, whose original routine analyses showed the high cation exchange of the soils.

laboratory had high capacities and were amorphous to x-rays. The capacities of the hydrous oxides of aluminum and titanium were so high that small amounts, if present, could have caused the high capacities observed in the soils. The differential thermal curves of the artificial colloidal hydrous oxides of aluminum contained various endothermic peaks similar to the unusual peaks of the soils.

This paper describes the properties of some of the soils and the artificial hydrous oxides.

ANALYTICAL PROCEDURES

Organic matter was destroyed by H_2O_2 before separation of clay fractions. If it was necessary to remove free iron oxides, Jeffries' procedure (3) was used. Soils were dispersed in aqueous NaOH of pH 10 by mechanical agitation. Clay of less than $2\ \mu$ equivalent diameter was separated with a bucket centrifuge.

It was found that sand and silt fractions had considerable exchange capacities, and it is likely that, because of incompatibilities in the isoelectric points of the materials present, aggregates of undispersed clay were retained in these coarser fractions. Separated clays, however, were shown by thermal analysis to be similar in composition to the material of the sands and silts, and conclusions reached should not be affected by the possible failure to attain complete dispersion.

A method recently developed in this laboratory was used for determining cation-exchange capacities on small samples by leaching with neutral normal potassium acetate, washing with 95 per cent alcohol, leaching out the potassium retained by the sample with neutral normal ammonium acetate, and determining the potassium in the leachate by flame spectrophotometry. Capacities determined by using potassium salts for the initial leaching have been shown by Golden *et al.* (2) to differ from those obtained with ammonium salts. Although very small samples were taken by the writers, cation-exchange values were reproducible to within 10 per cent. They agreed also to within this amount with the values obtained for larger samples by the more usual ammonium acetate method.

Differential thermal curves from 50° to 1000°C . were obtained by use of a metal block and a heating rate of approximately 10°C . per minute. Temperature values on the curves were measurable to within 4°C .

The x-ray examinations were made with a Philips Geiger x-ray spectrometer using an iron target tube.

PROPERTIES OF SOILS

Table 1 lists the properties of a number of soils of high cation-exchange capacity. Organic carbon contents of the untreated soils were between 2 and 5 per cent. Cation-exchange capacities of all samples were only slightly lowered after H_2O_2 treatment, showing that capacities due to organic matter were, in fact, very small.

Differential thermal curves of organic-freed soils closely resembled the curves of their clay fractions. Even after the deferration treatment, the clays resembled

TABLE 1
Properties of soils of Cook Island Group and their clay fractions

SAMPLE NO.*	LOCALITY	DEPTH in.	FRACTION†	CATION EXCHANGE CAPACITY‡ me./100 gm.	SiO ₂ /Al ₂ O ₃ MOLECULAR RATIO	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	TiO ₂ %	MgO %	CaO %	Na ₂ O %	K ₂ O %	MnO %	P ₂ O ₅ %	Cr ₂ O ₃ %	SUM OF OXIDES %	MINERALS IN CRYSTALLINE CLAY FRACTION
1	Atiu Island	0-3	A	22.0	0.29	1.88	11.20	74.48	9.11	0.49	tr.	tr.	tr.	0.08	2.64	0.23	100.11	Goethite, gibbsite anatase
	Atiu Island	0-3	B	10.5	0.43	7.19	28.22	55.29	6.81	0.50	1.37	—	—	0.04	—	—	—	
	Atiu Island	0-3	C	18.5	—	—	—	—	—	—	—	—	—	—	—	—	—	
2	Atiu Island	12-18	A	18.0	0.29	3.59	20.98	63.97	6.20	0.36	0.73	tr.	tr.	0.05	4.19	0.17	100.24	Goethite, gibbsite anatase
	Atiu Island	12-18	B	16.0	0.60	6.07	17.19	53.19	22.00	0.67	0.21	—	—	0.60	—	—	—	
	Atiu Island	12-18	C	16.0	—	—	—	—	—	—	—	—	—	—	—	—	—	
3	Atiu Island	3-9	A	36.0	1.13	21.61	32.43	31.31	6.87	0.76	2.76	—	—	0.30	3.76	0.13	—	Gibbsite, boehmite kaolin, anatase
	Atiu Island	3-9	B	23.0	1.02	24.64	41.00	29.25	5.11	—	—	—	—	—	—	—	—	
	Atiu Island	3-9	C	33.0	—	—	—	—	—	—	—	—	—	—	—	—	—	
4	Mangaia Island	0-6	A	25.0	0.89	16.67	31.96	39.96	6.37	0.92	0.59	0.10	0.08	1.87	1.32	0.07	99.91	Goethite, boehmite kaolinite, anatase
	Mangaia Island	0-6	B	16.0	1.00	19.58	33.20	38.55	5.05	0.67	0.09	—	—	1.36	1.50	—	—	
	Mangaia Island	0-6	C	22.0	—	—	—	—	—	—	—	—	—	—	—	—	—	
5	Mangaia Island	12-18	A	7.0	1.12	20.74	31.54	38.44	5.90	0.66	0.39	0.18	0.06	1.30	0.92	0.08	100.21	Goethite, boehmite kaolinite, anatase
	Mangaia Island	12-18	B	11.0	1.25	24.00	32.62	36.90	4.62	0.71	tr.	—	—	0.24	1.25	—	—	
	Mangaia Island	12-18	C	22.0	—	—	—	—	—	—	—	—	—	—	—	—	—	
6	Aitutaki Island	0-6	A	44.0	0.14	1.75	21.40	58.34	10.25	1.00	1.84	—	—	0.20	4.84	0.24	—	Gibbsite, anatase
	Aitutaki Island	0-6	B	28.5	0.12	2.00	29.49	58.81	9.70	—	—	—	—	—	—	—	—	
	Aitutaki Island	0-6	C	20.0	—	—	—	—	—	—	—	—	—	—	—	—	—	

* Samples 1 to 6 are Laboratory Nos. 5748A and C, 5749B, 5749A and B, and 5810 respectively. Sample 2 is subsoil of 1. Sample 5 is subsoil of 4.

† A, whole soil; B, <2 μ fraction, freed from organic matter; C, <2 μ fraction, freed from organic matter and iron oxides.

‡ Cation-exchange capacity figures are based on air-dried weight. Silicate analysis figures, in those cases where the sum of the oxides is listed, are percentages on ignited weight; in the remaining cases the figures are percentages of the sum of the constituents determined.

the soils in their high cation-exchange capacities and the distinctive endothermic peaks in their thermal curves. The materials causing high capacities in the soils were obviously still present in the clays. In the differential thermal curves the

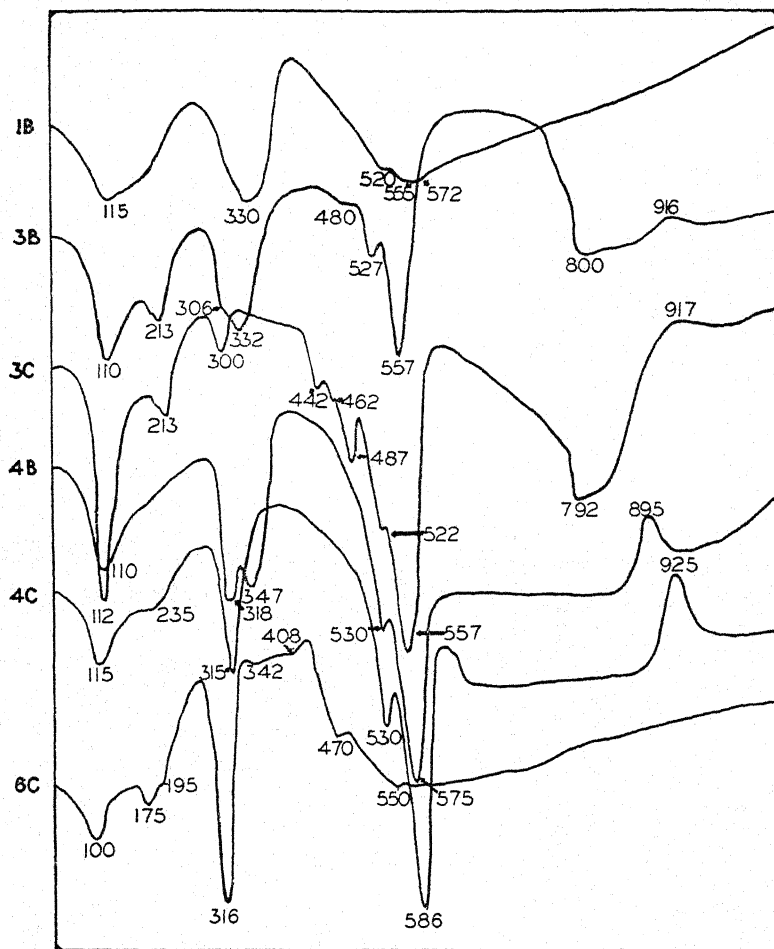


FIG. 1. DIFFERENTIAL THERMAL CURVES OF CLAYS

1B. Clay fraction of soil from Atiu. 3B. Clay fraction of soil from Atiu. 3C. Deferrated clay fraction of soil from Atiu. 4B. Clay fraction of soil from Mangaia. 4C. Deferrated clay fraction of soil from Mangaia. 6C. Clay fraction of soil from Aitutaki.

clays showed up the distinctive endothermic peaks somewhat better than did the soils. The thermal curves of the clays are shown in figure 1.

The curves include some peaks which can be identified as belonging to kaolin, gibbsite, and goethite. They contain also, in the range between 100° and 600°C., a number of endothermic peaks that do not usually occur in the curves of soil minerals.

Curves 3B, 3C, 4B, and 4C belong to the materials having silica-alumina ratios

near 1.0. They have endothermic peaks near 110°C. and in the region 550° to 590°C. and exothermic peaks in the neighborhood of 900°C. These peaks are produced by a kaolin type mineral intermediate between kaolinite and halloysite. Peaks between 300° and 318°C. are due to gibbsite. This mineral usually gives a marked endothermic peak at 330°C. The lower values for these samples may be due to differences in composition or to the lower amounts of gibbsite present, which would tend to make the peaks occur earlier. When present, kaolin and gibbsite show up clearly in the x-ray patterns.

Endothermic peaks between 330° and 350°C. are due to goethite. Berkelhamer (1) and other writers have reported an endothermic between 330° and 335°C. for this mineral. X-ray patterns confirmed the presence of goethite in some of the soils. In the other soils which contained no iron oxide crystalline to x-rays, similar peaks may be due to goethite of very fine particle size. The effect of deferration is to remove the peak due to goethite, as may be seen by comparing curves 3B with 3C, and 4B with 4C.

Besides the peaks attributed to kaolin, gibbsite, and goethite, the curves of all samples have unusual endothermics. Curve 3C, for instance, shows in addition to the peaks of kaolin and gibbsite a series of endothermic peaks at 200, 213, 442, 462, 487, and 522°C. Curve 6C is of particular interest. As the deferrated clay in this case consisted of approximately 80 per cent alumina, 15 per cent titanium oxide, and only 3 per cent silica, its peaks can be associated only with oxides of aluminum or titanium. This curve has, in addition to a peak at 316°C. due to gibbsite, a series of endothermic peaks at 175, 195, 342, 408, 470, and 550°C.

The soils and ferrated clays have phosphate contents up to 5 per cent. According to Manly (6), the thermal curves of various mineral phosphates have endothermic peaks in the range 100° to 600°C. There was no agreement, however, between the thermal curves obtained in this work and those of any of the fourteen phosphate minerals published by Manly. The possibility that phosphates cause the unusual peaks is eliminated, as the peaks are present in the curves of the deferrated clays (3C, 4C, and 6C of figure 1) where the phosphate content is less than 0.1 per cent as P_2O_5 .

Since known hydrous oxides of aluminum have endothermic peaks due to loss of lattice hydroxyl as far apart as 330°C. for gibbsite and 580°C. for diaspor, it seemed possible that amorphous hydrous oxides of aluminum might exist which had similar endothermic reactions in thermal analysis.

Electron micrographs of the deferrated clays showed that sample 6 contained apparently amorphous material of about 700 A. diameter. Sample 3 contained similar material and also some kaolin.

It was decided to investigate the properties of artificial amorphous oxides to determine whether their x-ray, differential thermal, and base-exchange characteristics are related to those of the material in these soils.

ARTIFICIAL HYDROUS OXIDES

The cation-exchange capacities of several hydrous oxides are listed in table 2. Samples 7 and 8 were prepared by dissolving 1 gm. of aluminum powder in

250 ml. of normal aqueous NaOH solution. After cooling, hydrous aluminum oxide was precipitated by CO₂ rapidly bubbled through the solution for 5 hours.

Sample 11 was prepared by dissolving 5 gm. of ferric ammonium sulfate in 200 ml. of water at 15°C. Hydrous ferric oxide was precipitated by adding excess of aqueous NH₄OH.

Sample 12 was prepared by making a saturated solution of potassium fluotitanate in water. Hydrous titanium oxide was precipitated by decomposing the salt with excess of aqueous NH₄OH at a temperature near boiling.

The preparations described and the determinations of capacity were repeated a number of times. The exchange capacities of the resultant hydrous oxides were reasonably reproducible. The hydrous oxides of iron were also precipitated at boiling point and boiled for various lengths of time up to 1 hour, since it was

TABLE 2
Cation-exchange capacities of hydrous oxides

SAMPLE NO.	HYDROUS OXIDE	ORIGIN	CATION-EXCHANGE CAPACITY <i>me./100 gm.</i>
7 & 8	Colloidal hydrous aluminum oxide	Precipitated cold by CO ₂ from sodium aluminate	350
9	Colloidal hydrous aluminum oxide	Precipitated cold by ammonia from aluminum nitrate	0
10	Alumina "trihydrate"	British Aluminum Co.	0
11	Colloidal hydrous iron oxide	Precipitated cold by ammonia from ferric ammonium sulfate	25
12	Colloidal hydrous titanium oxide	Precipitated at 100°C. by ammonia from potassium titanium fluoride	190
13	Silica gel	British Drug Houses	34

suggested in the literature that oxides of varying degree of hydration could be produced in this way. There was no significant variation in the exchange capacity of the different precipitates.

The x-ray diffraction pattern of sample 10 corresponds with that of gibbsite. The other oxides were amorphous to x-rays.

The differential thermal curves are shown in figure 2. The curves of the hydrous aluminum oxides, 7 to 10, resemble those of the clays in figure 1, in having endothermic peaks between 100° and 600°C. The curves of the other hydrous oxides are not like those of the clays. This strengthens the suggestion that the unidentified endothermic peaks in the curves of the clays were due to hydrous aluminum oxides.

Evidence such as that published by Weiser and Milligan (8, pp. 227-237) and others has demonstrated that the degree of crystallinity of such hydrous oxides varies with the method of preparation. Even material amorphous to x-rays may be shown by electron diffraction to have varying degrees of crystallinity. Oxides of aluminum, iron, titanium, and silicon which were crystalline to x-rays, like

the gibbsite of hydrous oxide sample 10, had negligible capacity. Possibly sample 9, which although amorphous to x-rays has low capacity, would show structure to electron diffraction.

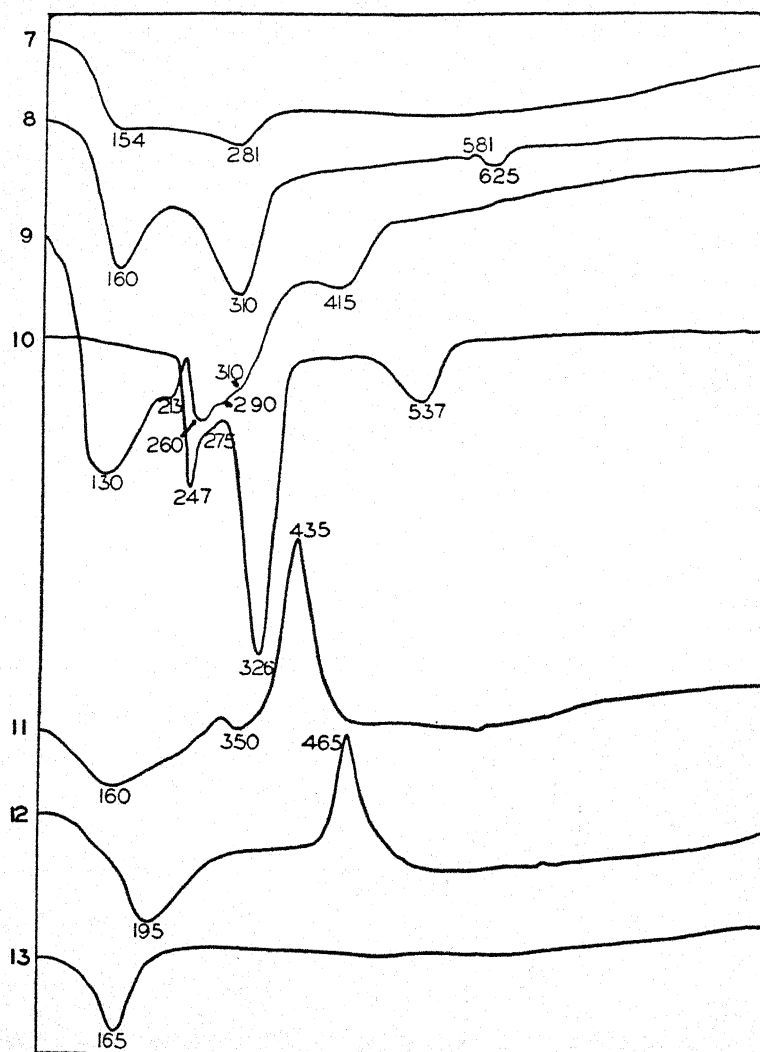


FIG. 2. DIFFERENTIAL THERMAL CURVES OF ARTIFICIAL HYDROUS OXIDES
7, 8, and 9. Hydrous aluminum oxides. 10. "Alumina trihydrate." 11. Hydrous iron oxide.
12. Hydrous titanium oxide. 13. Silica gel.

Electron micrographs showed that sample 8 consisted mostly of amorphous material less than 200 A. in diameter. Sample 10 consisted of flakes about 1 μ in diameter.

It may be suggested that the properties of precipitated gels change consider-

ably with age. The x-ray patterns and exchange capacities of the oxides listed in table 2 were not altered during the several weeks that this work was in progress.

The evidence presented indicates that the unusual endothermics in the differential thermal curves of these soils are due to various hydrous aluminum oxides. Some of these oxides have low exchange capacities, whereas others have very high capacities. The latter high-capacity amorphous hydrous aluminum oxides are responsible for the high capacities of the soils described.

Since the thermal curves of the soils and clays do not have the characteristic exothermic peaks at 435° or 465°C. due to rearrangement of the oxides of titanium and iron respectively, these oxides are not present and do not contribute to the capacities.

Although amorphous silica is not thought to be a contributing factor in the capacity of the soils, it is not definitely eliminated in the soils of higher silica content. Its thermal curve and exchange capacity figure are therefore included.

DISCUSSION

Cation-exchange capacity was attributed by early workers to colloidal oxides. The comparatively recent demonstration by x-ray diffraction that crystalline aluminosilicate clay minerals of high exchange capacity exist caused the earlier view to be largely abandoned. Although recent work generally accepts the possibility that amorphous clays occur in soils, there is little information regarding their nature, extent, or properties.

Some soil colloids from Hawaiian soils described by Kelley and Page (4) were reported to have high exchange capacity, contain no montmorillonite, and show only weak x-ray lines. These writers established that "amorphous appearing material" was present. They mentioned specifically amorphous iron oxide, silica, and precipitated permutite-like substances. It is possibly to the latter that they attributed the cause of high capacity. Since permutites have very high silica-alumina ratios, they could not be important in the soils of low silica content described in this paper.

Allophane, which is also amorphous to x-rays and has a low silica-alumina ratio, is not a constituent of these soils, as its characteristic peaks are absent from their thermal curves.

SUMMARY AND CONCLUSION

The evidence of x-ray diffraction, differential thermal analysis, exchange capacity estimations, and chemical analysis suggests that the cation-exchange capacity of some soils of the Lower Cook Islands Group is due mainly to amorphous colloidal hydrous oxide.

Artificially prepared amorphous hydrous oxides of aluminum and titanium can have very high cation-exchange capacities. The corresponding oxides of iron and silica have much lower though still considerable capacities. All of the artificial hydrous oxides have distinctive differential thermal curves.

The thermal curves of the soils, clays, and artificial hydrous aluminum oxides contain multiple endothermic peaks between 100° and 600°C., but they differ

from the curves of hydrous oxides of iron, titanium, and silicon. This suggests that the principal exchange material in these soils is amorphous hydrous aluminum oxide.

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INFLUENCE OF THE HANDLING OF SUGAR CANE TRASH ON YIELDS AND SOIL PROPERTIES

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Received for publication October 30, 1951

The proper handling of trash in sugar cane fields is of great importance to Puerto Rican growers because of its direct bearing on the cost of production, yield of cane, and such varied aspects of the physical and chemical properties of the soil as erosion, infiltration, organic matter content, and structure. The handling of trash is an essential part of the agronomic practices of growing sugar cane. Proper management can mean greater profits to the sugar cane grower, not only through savings in labor costs but also through increases in yields.

Sugar cane trash is the material left on the surface of the ground after harvest. It consists of all the leaves and the upper immature part of the stalk. Hardy and Evans (5) estimated that a ton of trash was produced for every 4 tons of green-millable cane. In 1949, when 10,998,026 tons of cane were milled in Puerto Rico with an average acre-yield of 31.2 tons (8), this meant the disposal of almost 8 tons of dry sugar cane trash containing 93 pounds of combined nitrogen per acre (9). If handled properly, this trash becomes an asset; if misused, it can become a liability to the sugar cane grower.

Utilization of the trash presents practical difficulties. Many sugar cane planters in Puerto Rico, Hawaii, and Louisiana simply burn it. The trash is very bulky and is difficult to plow under for a new crop or to manage in the cultivation of the ratoon crop. If it is buried or plowed under deeply, decomposition may be too slow, and the effective use of soil nitrogen is hindered. Should the trash remain undecomposed, it may serve to protect the dormant stage of insects injurious to the cane, and under conditions of excessive moisture and low temperature, its presence may increase the infection of the cane by facultative parasitic soil fungi.

Bonnet *et al.* compared the effect of leaving the trash as a mulch and of burning it for four crops of sugar cane (1944-1948) grown in a lateritic soil with a 40 per cent slope. No significant differences in yields were found between treatments. Highly significant differences, however, were found in soil losses, the unmulched plots losing about 11 times more soil than the mulched ones (3).

Bonazzi (1), Bonnet (2), and Sturgis (10) reported that incorporation of sugar cane trash in the soil increased the total soil nitrogen as it decomposed. They also found that addition of inorganic nitrogen to the trash in the soil hastened its decomposition.

PROCEDURES

To determine the effects of different methods of handling the trash on yields of sugar cane, experiments were undertaken at Río Piedras on Vega Alta silty clay in 1945.

The procedure for the handling of the trash for each treatment were as follows:

Trash burned: The trash was spread evenly through the plot and then burned.

Trash buried: A furrow was made about 1 foot deep between rows; the trash was placed in the furrow and covered with soil.

Trash aligned: The trash was aligned in alternate banks or rows.

The treatments were repeated every year after each harvest. The experiment consisted of a simple randomized block in which each treatment was replicated 20 times on plots 150 feet long by 20 feet wide, with the cane rows 4 feet apart. The variety of cane used was P.O.J. 2878. The field as a whole received an application of 1,200 pounds of a 15-3-10 fertilizer every year.

On April 2, 1951, a soil profile was taken with a Kelley soil sampling machine (6) to a depth of 72 inches in the middle of the experimental field. It revealed a very dark grayish brown (10 YR 4/2) surface about 11 inches deep with a moderately developed angular structure. The 12-29-inch layer was yellowish red (5 YR 5/8) with considerable red mottling and a moderately developed subangular structure. The 30-72-inch layer was a yellowish brown (10 YR 5/8) silty clay loam with red and gray mottling.

Infiltration tests were run in the field, and samples were taken from each plot for laboratory analysis. Bulk composite samples were taken from the topmost 6 to 8 inches of the soil. Each composite consisted of 10 samples. Undisturbed cores, 3 inches in diameter and 3 inches in length, were also taken at two depths, 0-3 and 3-6 inches, with a Bradfield soil sampler. To determine the infiltration rate, the buffer-compartment method, as outlined by Nelson and Muckenhirn, was used (7). Iron rings, 9, 18, and 27 inches in diameter, were jacked into the soil. A $\frac{1}{4}$ -inch head of water was maintained within the center ring by means of a self-dispensing calibrated 2,000-ml. burette. The same hydraulic head was maintained in the outer compartments to minimize lateral movement of water from the inner ring, where measurements were taken hourly. The tests were run for 8 consecutive hours.

Permeability measurements were made in undisturbed soil cores by recording the rate at which water moved through a column of saturated soil at a known head. In the measurement, special equipment was used as described by Smith, Furhman, and Silva.¹ Quick drainage was determined by placing the saturated core in a Büchner funnel, setting up a 60-cm. tension, and measuring the water drained out at the end of 15 minutes. The water removed and retained at pF 1.78 was measured by bringing the soil core to equilibrium with a 60-cm. tension and determining the variation in weight of the core. The maximum saturation was calculated from these data.

The soil core was finally dried in the oven at 110°C. As the sampler used had a definite known volume, the bulk density was calculated by dividing the net dry weight of soil by its volume. The pore space was then calculated by assuming a specific gravity of 2.65. As used in this paper, the air porosity is the dif-

¹ Simple procedures for studying cores collected with the Kelley (Utah) sampling machine. BPI-SCS Cooperative Research Project Report 181 (mimeo).

ference between the theoretical pore space and the volume of water retained at pF 1.78.

The pH was determined electrometrically by means of a Macbeth pH-meter. Total nitrogen was determined by the standard Kjeldahl method, and organic matter by the simple colorimetric Schollenberger technique. The carbon-nitrogen ratio was subsequently calculated from the data.

RESULTS AND DISCUSSION

Yield Data

The yields for a plant cane and six ratoon crops are presented in table 1. The results from the plant cane were utilized as a uniformity test of the field, because the various treatments were not applied until after the plant cane was harvested. There were no significant differences between treatments or plots,

TABLE 1

Mean yields of available 96° sugar of a plant cane and 6 ratoon crops at Río Piedras

TREATMENTS	MEAN AVAILABLE 96° SUGAR PER ACRE							
	Plant cane	First ratoon	Second ratoon	Third ratoon	Fourth ratoon	Fifth ratoon	Sixth ratoon	Mean yield of 6 ratoon crops
	<i>cwt.</i>	<i>cwt.</i>	<i>cwt.</i>	<i>cwt.</i>	<i>cwt.</i>	<i>cwt.</i>	<i>cwt.</i>	<i>cwt.</i>
Trash burned...	55	106	127	109	107	114	91	109
Trash buried...	54	107	125	108	109	115	96	110
Trash aligned...	54	106	127	105	105	122	99	111
L.S.D. at 1% level.....	5.4	8.0	11.1	9.2	8.6	8.6	7.3	6.1
L.S.D. at 5% level.....	4.0	6.0	8.3	6.9	6.4	6.5	5.4	4.6

indicating that the experimental site selected had no appreciable differences in fertility that might tend to obscure the results of the various treatments. This uniformity in fertility was of importance, in that the differences obtained by subsequent treatments could be attributed to the effect of the treatment rather than to soil variations.

No significant differences in the yield of available 96° sugar in hundred-weights per acre were obtained for the first four ratoon crops. Significant differences in yields were obtained in the fifth and sixth ratoons. In the fifth ratoon the yield for the aligned-trash treatment was significantly higher at the 5 per cent level than for the burned- and buried-trash treatments. For the sixth ratoon, the difference between the aligned-trash and the burned-trash increased to significance at the 1 per cent level. There was no significant difference between yields for the burned- and buried-trash treatments.

Special attention should be given to the results of the fifth and sixth ratoons of this experiment. After 5 years of continuous cultivation, the influence of the treatments begin to produce significant differences in yields. In the first few

years these differences were not appreciable, as judged by yield data, and this tended to give a false picture. With increases in time of cultivation, these differences accumulated and appeared as effects on yields. Some of the changes in soil properties caused by treatments which influenced the yields are discussed under soil data.

It is easy to burn sugar cane trash. The decreases in yields caused thereby are slow and difficult to measure. The burning does, however, lower yields when practiced over a long period. The grower must come to realize that, when the flames start to consume the trash in his fields, they may also be destroying the ability of his soil to produce higher sugar yields. In the experiments described here the burning of the trash represented a loss of 8 hundredweight of sugar per acre per year in the last two ratoon crops, as compared with yields from the aligned-trash treatment.

The burned- and buried-trash treatments were followed more rapidly by growth of weeds than the aligned-trash treatment. This means the cultivation costs will be higher in the burned- and buried-trash plots than in aligned-trash plots.

The burying or burning of the trash produced no increase in yields, and over a period of years gave lower yields than the normal practice of aligning trash. Burying the trash is not cheaper than aligning it. Burning is cheaper than aligning or burying, but continued burning lowers yields, increases soil erosion, and results in higher weeding costs.

Soil Data

The chemical analyses of the soils taken from the Río Piedras trash-handling experimental field are shown in table 2. The general pH values fluctuated between 4.5 and 6.2 with a mean value of pH 5.0 for all treatments combined. There were no significant differences between the means of the treatments.

There was no significant difference between the mean nitrogen contents whether the trash was burned, buried, or aligned. Apparently, the addition of 180 pounds of nitrogen per acre per year in the fertilizer application was sufficient for all crop and soil needs, and there was no nitrogen accumulation in the trash plots by fixation. The influence of the trash on soil nitrogen might have been felt more if such heavy additions of nitrogen fertilizer were not made to the sugar cane.

There were highly significant differences in the organic matter content between the means of the treatments. The plots on which the trash was either buried or aligned had a much higher organic matter level than did those on which the trash was burned. After 6 years of establishing the treatment differentials, the accumulated differences were clearly marked.

Difficulties were encountered in sampling for nitrogen and organic matter determinations in the three treatments. Although all surface trash was removed before sampling, the 10 samples taken within the plot showed variation. These differences were responsible for a high standard error. But, despite variations of the soil within the individual treatments, there was significant difference in organic matter content of the soil attributable to the treatments used.

The plots where the trash was aligned or buried had received not less than 8 tons of trash to the acre after each harvest, which amounts to 48 tons during the cycle of one plant crop and five ratoons. Accumulation of organic matter in the soil is a slow process. Assuming the weight of the acre-furrow slice to be 2 million pounds, the organic residues added during the crop cycle should amount to 4.8 per cent. It must be remembered, however, that a large proportion of the organic matter added is decomposed by the microorganisms of the soil and releases essential nutrients for plant growth. Furthermore, the sugar cane trash has a wide C/N ratio of about 40:1 (2). By the time the residues become an integral part of the soil, the ratio is usually narrowed down to 10:1. Thus the 48 tons of organic material become 12 tons of organic matter with a C/N ratio of 10:1, equivalent to 1.2 per cent of organic matter in the plowed layer. This decomposition of the trash is rapid under the climatic conditions of the tropics. In spite of the apparently large applications of plant residues to the plots where the trash was buried and aligned as compared to those where

TABLE 2

Mean pH, nitrogen, organic matter, and C/N ratio of soil from the sugar cane trash-handling experimental field at Rio Piedras

TREATMENTS	pH	NITROGEN	ORGANIC MATTER	C/N RATIO
		<i>per cent</i>	<i>per cent</i>	
Trash burned.....	5.1	0.145	1.43	5.7
Trash buried.....	4.9	0.149	1.83	7.8
Trash aligned.....	5.0	0.144	1.70	7.0
L.S.D. at 5% level.....	0.18	0.018	0.22	1.7
L.S.D. at 1% level.....	0.24	0.024	0.30	2.3

the trash was burned, the increases in organic matter content observed in the former over the latter two were of the magnitude of only 0.4 and 0.3 per cent, respectively. There were no significant differences between the buried- and aligned-trash treatments.

The difference in C/N ratio between the buried- and the burned-trash treatments was significant. In general, the ratio was narrower in the plots where the trash was burned. In the other plots, which received large amounts of carbonaceous plant material for 6 consecutive years, the ratio was a little wider. All these ratios considered together, however, were less than 10:1, which indicates that the trash had decomposed quickly. No wide C/N ratios indicative of slow decomposition were observed. The yearly application of fertilizer ensures an adequate supply of nitrogen for both microorganisms and plants during the early critical stages of crop growth.

Table 3 gives the mean infiltration rate of the soil as determined for each 8 hours on plots where the sugar cane trash had been handled differently for the last 6 years.

In general, the infiltration rate was slower in the plots where the trash was burned than in those where it was either buried or aligned. The buried-trash

plots, which were disturbed mechanically every year in making a furrow between cane rows, gave the highest rate of infiltration. This high rate of infiltration is especially beneficial in Puerto Rico where heavy rainfalls of short duration are not uncommon. Soils with the lower infiltration rate cannot absorb as much water, and most of the rain is lost as runoff. The possibility of obtaining significant differences in filtration rates with larger accumulations of organic matter in the soil remains to be confirmed in the future.

TABLE 3

Water infiltration rate of soils where sugar cane trash was burned, buried, or aligned for 6 consecutive years

TREATMENT	INFILTRATION RATE AFTER INDICATED TIME							
	1 hour	2 hours	3 hours	4 hours	5 hours	6 hours	7 hours	8 hours
	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>
Trash burned	7.54	2.76	2.00	1.76	1.98	1.55	1.35	1.40
Trash buried	14.77	7.06	4.04	3.56	3.18	2.50	2.96	2.38
Trash aligned	9.93	4.36	3.10	3.05	2.78	2.47	2.34	2.00
L.S.D. at 5% level.								3.11

TABLE 4

Permeability and other soil-moisture data gathered from soil cores collected from the sugar cane trash-handling experimental field at Río Piedras

TREATMENT	SAMPLING DEPTH	PERMEABILITY PER HOUR	WATER DRAINED AT 60 CM. IN 15 MINUTES	MAXIMUM SATURATION	WATER REMOVED AT pF 1.78	WATER RETAINED AT pF 1.78
	<i>inches</i>	<i>inches</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Trash burned	0-3	0.51	2.65	50.92	5.42	44.97
	4-7	1.60	0.77	51.80	2.30	49.40
Trash buried	0-3	0.44	1.38	49.90	3.58	46.15
	4-7	4.00	1.15	50.47	2.65	47.80
Trash aligned	0-3	0.80	2.25	54.70	4.70	50.00
	4-7	6.67	0.98	52.42	2.68	49.70
L.S.D. at 5% level.....	0-3	0.53	1.51	3.42	2.01	4.39
	4-7	9.39	0.48	1.72	1.12	1.67

In addition to the infiltration rates determined under field conditions, a number of undisturbed soil cores were taken for soil-moisture studies under laboratory conditions. The results are reported in table 4.

In general, there were no outstanding significant differences in the moisture characteristics of the soils representing the various trash-handling treatments. Some trends, however, should be pointed out. Perhaps they will become significant with the larger differences in organic matter levels to be expected in coming

years as a result of the various methods of handling trash. The movement of water as indicated by permeability measurements seems to be slower in the burned-trash plots than in the others. The plots where the trash was aligned in alternate rows seem to have a higher moisture content at maximum saturation than those otherwise treated. More water was removed from soil cores that reached equilibrium with a 60-cm. tension when they came from the plots where the trash was burned than from cores coming from plots where it was either buried or aligned.

The last column of table 4 indicates that the upper layer of soil in the trash-aligned plots may retain more water at low tensions than that of the plots treated differently. The trash-burned plots retained the least volume of water at pF 1.78. In all probability this water is readily available, the plants being able to remove it quickly, until tensions reach the vicinity of the permanent

TABLE 5
Bulk density, pore space, and air capacity of soils from the sugar cane trash-handling experimental field at Rio Piedras

TREATMENT	SAMPLING DEPTH	BULK DENSITY	PORE SPACE	AIR POROSITY (PORE SPACE-WATER RETAINED AT pF 1.78)
	<i>inches</i>	<i>gm./ml.</i>	<i>per cent</i>	<i>per cent</i>
Trash burned	0-3	1.26	52.45	7.48
	4-7	1.28	51.47	2.07
Trash buried	0-3	1.26	52.25	6.10
	4-7	1.28	51.68	3.88
Trash aligned	0-3	1.19	55.12	5.12
	4-7	1.26	52.63	2.93
L.S.D. at 5% level	0-3	0.097	3.98	—
	4-7	0.048	2.10	—

wilting percentage (pF 4.2). Although the soil differences are not significant, there is an indication that over a period of years trash-burning is a detrimental practice so far as total water retention is concerned; perhaps the total available water is also reduced. This may have a bearing upon cane and sugar yields. The trash-aligned treatment had been reported previously to produce significantly higher sugar yields than either of the other two treatments, at least in the fifth and sixth ratoon crops. No significant differences were observed in the previous four crops in the cycle. The accumulation of organic matter in the soil with the consequent, although slow, change in the physical character of the soil, may serve to explain yield differences.

Table 5 presents data on bulk density, total porosity, and air porosity of soils taken from the variously treated plots at the trash-handling experimental field. The general bulk-density values ranged from 1.01 to 1.31 gm. per milliliter for the combined treatments, with mean values of 1.26 gm. for both the burned-

and buried-trash treatments and 1.19 for the aligned-trash treatment. The mean porosity value for all plots was 52.54 per cent by volume, with deviations of only 2.54 per cent above or below it. The air porosity was higher for the burned-trash plots and was progressively reduced through the buried- to the trash-aligned plots. The air porosity was in inverse relationship to the water porosity (water retained at pF 1.78), the total pore space being of more or less constant magnitude. The incorporation of large quantities of organic residues in a continuous, steady way for a number of years probably induces a better state of aggregation and consequently the formation of a large proportion of microaggregates capable of holding a great deal of water at relatively low tensions. This fact has been substantiated by Browning and Milan (4) and others who found a significant increase in aggregation with each unit increase in organic matter.

There are changes in soil structure attributable to the method of handling the sugar cane trash. These changes make themselves felt by their influence on yields of sugar cane. Despite the high annual fertilizer applications, the original high productivity of the sugar cane in the trash-burned treatment is not maintained after the fifth ratoon, and yields begin to decline significantly. If high productivity is to be maintained in sugar cane fields over a period of years, the physical conditions of the soil as influenced by trash handling must be taken into consideration.

SUMMARY

Experiments on handling sugar cane trash were set up at Río Piedras to determine the effect on cane yields and soil properties.

The treatments conducted on a plant cane and six ratoons consisted of burying the trash, burning the trash, and aligning it in alternate rows.

There was no difference in sugar cane yields that could be attributed to any of the treatments until the fifth and sixth ratoon. Here highly significant differences in yields were obtained from aligning trash as compared with burning or burying it.

Field observations indicated that weeding costs were greater with the burned- and buried-trash practices than when the trash was aligned.

After the sixth ratoon crop was harvested, infiltration tests were run in the field, and bulk and core samples were taken for laboratory analysis. No significant differences were observed between the mean pH and the total nitrogen values for the various treatments. The mean organic matter content of the trash-burned plots was significantly lower (at the 1 per cent level) than that of the buried- and aligned-trash plots. The C/N ratio was narrow in all cases, but lower for the burned-trash treatment.

Differences between the mean infiltration rates at the eighth-hour run for the burned-, aligned-, and buried-trash treatments were not significant. No significant differences were observed between the means of the various physical measurements; namely, permeability, quick drainage, maximum saturation, water removed, and water retained at pF 1.78, bulk density, total porosity, and air porosity.

Some trends observed may become significant with continuous accumulation of organic matter in the buried- and aligned-trash treatments. Permeability, for instance, appeared to be slower in the burned-trash plots. The upper layer of the trash-aligned plots seemed to retain more water at low tension than did that of the plots treated otherwise.

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USE OF MEAN SOIL MOISTURE TENSION TO EVALUATE THE EFFECT OF SOIL MOISTURE ON CROP YIELDS

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Received for publication September 4, 1951

This paper is a report of the first season's application of a new technique for measuring mean integrated soil moisture tension (6). The technique has been used for the dual purpose of giving a criterion for irrigation and of measuring the effect of soil moisture on crop yields.

Soil moisture tension was measured by use of tensiometers to indicate tensions up to 0.7 atmosphere and calibrated plaster blocks to indicate higher tension.

EXPERIMENTAL APPLICATION

Plaster blocks were calibrated in terms of moisture tension by placing some of the blocks in a pressure membrane apparatus (4), covering them with a thin layer of soil, and bringing the leads out through spark plugs placed in the walls of the pressure membrane apparatus. The calibration curve attained in this manner is given in figure 1. This calibration was used as a basis for making a new dial for the resistance bridge in order to take readings directly in moisture tension in the field. Other moisture-measuring devices using both conductivity bridge and the ohmmeter described by Coleman and Hendrix (2) have subsequently been calibrated with good success. Some of the difficulties experienced in this type of calibration are discussed by Haise and Kelley (3) and by Tanner, Abrams, and Zubriski (5). Soil was placed in the pressure membrane unit to establish better contact between blocks and membrane and to make the environment outside the block similar to field conditions, thus compensating in part for the lines of electrical force that extend outside the block and into the soil. Since these lines of force are present in the field installation, to eliminate them in the calibration would introduce errors.

Both in the field and in the laboratory, the blocks increased in resistance at the same moisture tension in the soil when they were successively allowed to wet and dry in normal use. It is believed that this change in calibration results from recrystallization of gypsum in the plaster blocks with successive wettings and dryings, which results in a change of pore size distribution in the blocks. This problem is being studied to find a means of correcting the drift. For this study, however, changes were made in the calibration at frequent intervals to correct for the drift. It is possible that the more costly nylon blocks of Bouyoucos and Mick (1) or the fiberglass blocks of Coleman (2) or some other type block will eliminate this difficulty.

¹ Research reported herein is supported by Regional Research project W-9 with eleven western states; Soil Conservation Service (Research); Bureau of Plant Industry, Soils, and Agricultural Engineering; Utah Idaho Sugar Company; and Amalgamated Sugar Co. cooperating.

In an experiment with crops in a rotation involving both fertilizer and moisture variables, gypsum blocks were placed in the highest fertility plot in each

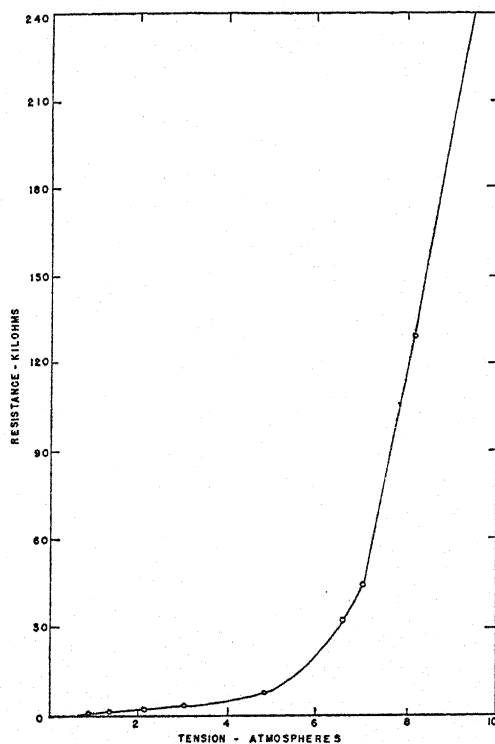


FIG. 1. CALIBRATION OF SOIL MOISTURE BLOCKS IN TERMS OF SOIL MOISTURE TENSION

moisture treatment at the time of seeding the crop in all cases. The number of blocks and distribution with depth for the various crops were as follows:

CROP	DEPTH OF PLACING BLOCKS (INCHES)	NO. OF BLOCKS PER PLOT
Potatoes	3, 6, 12, 18, 24	5
Sugar beets	3, 6, 12, 18, 24, 30, 36, 42, 48	9
Barley and 1st year alfalfa	6, 12, 18, 24, 30, 36, 48, 60	8
2nd year alfalfa	6, 12, 18, 24, 30, 36, 48, 60	8

Readings were taken of the moisture tension on each block at periodic intervals. All blocks placed in the soil of any one crop were read the same day. The average interval between successive readings on any one block was 4 days.

Soil moisture tensiometers of the manometer type were placed in all plots that were maintained at low and medium low tensions. The instruments were placed at 6-inch and 12-inch depths in the near vicinity of the gypsum blocks in the same plots. Readings were made daily except Sundays and holidays beginning at 8:00 a.m.

Because of the low precision of the gypsum blocks at low moisture tensions

(fig. 1) tensiometer data were used wherever possible in this range. The blocks were installed only as a precaution. In the field, tensiometers at field capacity indicated moisture tension of 0.10–0.12 atmospheres, which is about 0.3 to 0.4 atmosphere less than indicated by blocks. To compare data from both blocks and tensiometers, the value 0.4 has been subtracted from all block readings.

The soil used was Millville loam having an osmotic pressure of the saturation extract between 0.13 and 0.29 atmospheres, depending on depth of measurement. No attempt has been made in this study to combine this small osmotic effect with soil moisture tension to obtain the integrated soil moisture stress.

The method described for calculating the mean integrated soil moisture tension is the approximate mean weighted soil moisture tension previously reported (6).

PUNCH CARD ANALYSIS

Each reading of moisture tension from both blocks and tensiometers was recorded on an I.B.M. card. The cards were taken daily to the tabulating room, where the data were punched into the cards and analyzed.

The daily analysis consisted of a tabulation and listing of the observed tension of each block in each plot. The observed tensions were then totaled with respect to depth for each plot, thus completing the summation with respect to depth (6). An example of such a tabulation is given in table 1.

By observing the depth to which water was being withdrawn from a plot it was possible to estimate the depth of rooting of the plant. For example, on both plots 114 and 445, moisture was being withdrawn to a depth of 48 inches as shown by high tensions to that depth. Plots 233 and 344 had been watered recently; consequently, they did not show this characteristic. The data in table 1 also shows that plot 114 had received insufficient water at its last irrigation, as indicated by higher moisture tension from 24 to 42 inches than for 0 to 24 inches. The total of each plot indicates the relative dryness of the plot, the higher numbers indicating high tension which occurs in dry plots.

Daily readings from two tensiometers per plot in the low and medium-low tension plots were similarly summarized but, because of the low tension maintained, could not be used to calculate depth of rooting of plants.

Criterion for Irrigation

Plots were irrigated when the daily total reached a figure determined by the crop, the time of year, and the moisture level of the particular plot. The level of moisture established before the crops were planted was to irrigate all crops when the average moisture tension in the root zone approached permanent wilting, which was about 7.8 atmospheres as measured in the field in moisture level 1; when two-thirds the available moisture had been used, or 4 atmospheres tension had been reached in moisture level 2; when one-third available moisture had been used, or 0.6 atmosphere had been reached in moisture level 3; and when the soil dried to 0.2 atmosphere tension in moisture level 4.

The relative depth of the root zone was determined from the daily report, as previously explained, and was different for each crop at different times of the season. As the depth to which crops were removing water from the soil was

TABLE 1

Daily report of moisture tension on high-tension sprinkled plots of sugar beets on September 18, 1950, as shown by plaster blocks

DATE	CROP	MOISTURE TREATMENT	PLOT NO.	DEPTH OF READING	NUMBER OF BLOCKS	MOISTURE TENSION	
261	SB	1S	114	<i>in.</i>	9	<i>0.1 atm.</i>	
				03		34	
				06		31	
				12		23	
				18		30	
				24		50	
				30		54	
				36		52	
				42		50	
				48		32	
				Total		356	
		1S	233	03	9	37	
				06		43	
				12		31	
				18		25	
				24		20	
				30		19	
				36		15	
				42		16	
				48		15	
				Total		221	
		1S	344	03	9	16	
				06		18	
				12		20	
				18		13	
				24		13	
				30		14	
				36		12	
				42		13	
				48		15	
				Total		134	
		1S	445	03	9	35	
				06		62	
				12		55	
				18		63	
				24		61	
				30		63	
				36		55	
				42		62	
				48		52	
				Total		508	
		Grand Total				36	1,219

known, the number of blocks involved was determined and the tension attained at the moisture level desired was multiplied by the number of blocks in the

wetting zone to give the minimum daily total value at which irrigation should be applied. With this technique, the following criteria were set up on the dates indicated and were used until the next date listed:

DATE	MOISTURE LEVEL	DEPTH OF DRYING	METHOD OF MEASURING	NUMBER OF BLOCKS	MEAN TENSION DESIRED	DAILY TOTALS
		(inches)			(atm.)	(0.1 atm.)
June 16, Potatoes	1	12	Blocks	3	7.8	230
	2	12	Blocks	2	4.0	080
	3	12	Tensiometers	2	0.6	012
	4	12	Tensiometers	2	0.2	004
June 16, 2nd year alfalfa	1	48	Blocks	7	7.8	556*
	2	48	Blocks	7	4.0	280
	3	12	Tensiometers	2	0.6	012
	4	12	Tensiometers	2	0.2	004
July 6, Potatoes	1	12	Blocks	3	7.8	230
	2	12	Blocks	3	4.0	120
	3	12	Tensiometers	2	0.6	012
	4	12	Tensiometers	2	0.2	004
July 6, 2nd year alfalfa	1	60	Blocks	4	7.8	600
	2	48	Blocks	7	4.0	300
	3	12	Tensiometers	2	0.6	012
	4	12	Tensiometers	2	0.2	004
July 6, Sugar beets	1	18	Blocks	4	7.8	300
	2	12	Blocks	3	4.0	100
	3	12	Tensiometers	2	0.6	012
	4	12	Tensiometers	2	0.2	004
July 6, 1st year alfalfa and new alfalfa	Irrigate all new stands of alfalfa when sum of tensions at all depths reaches 100.					
August 10, 2nd year alfalfa	1	Same as on July 6		6	2.3†	140
	2	Same as on July 6				
	3	30	Blocks			
	4	Same as on July 6				
Sugar beets	1	36	Blocks	7	7.8	546
	2	36	Blocks	7	4.0	280
	3	12	Tensiometers	2	0.6	012
	4	12	Tensiometers	2	0.2	004
Potatoes	Same as on July 6					
New alfalfa	Same as on July 6					

* Because of extremely low tension early in the season, the value used here was 450, but no plot was irrigated until the criteria were changed. Sugar beets same as potatoes at this stage (June 16).

† This level was raised because of small differences that occurred between 3 and 4 as a result of inadequate sampling of root zone by two tensiometers.

This method proved quite satisfactory as a technique for determining the time to irrigate. Some difficulty in sampling was experienced, however, as a result of unequal distribution of moisture on the plots; for this reason consideration is being given to installing all blocks at the same position relative to the

TABLE 2
Calculation of the mean soil moisture tension for high tension sugar beet plot 114

DATE	WEIGHTING FACTOR ($d_{i+1} - d_i$)	TOTAL WEIGHTED TENSION* $\sum_{j=0}^9 (d_{i+1} - d_i) T_{ij}$
		atm.
160	8	21.6
168	8	33.6
173	5	30.5
177	4	31.2
180	3	24.9
186	6	87.6
188	2	34.4
192	4	78.0
195	3	78.0
198	3	95.4
201	3	107.7
205	4	160.4
212	7	173.6
216	4	84.8
221	5	109.0
227	6	183.0
233	6	292.8
237	4	227.6
242	5	176.0
247	5	129.0
251	4	90.6
255	4	90.8
261	6	213.6
265	4	177.6
Total	113	2,731.7

$$\text{Mean soil moisture tension} = \frac{2731.7}{9 \times 113} = 2.69 \text{ atm.}$$

* The total weighted tension is the sum of the products of the weighting factor by the observed tension for each of the 9 depths: 3, 6, 12, 18, 24, 30, 36, 42, and 48 inches.

sprinkle pipe or the center line of the plot in future studies. To test sampling variability, duplicate sets of blocks will be placed in some plots in future studies.

Mean Soil Moisture Tension

The total for each moisture plot on each day was multiplied by the weighting factor (6), which is the time interval between successive observations, and

totalled for time. The mean integrated soil moisture tension was calculated for each plot according to the equation

$$T_{pm} = \frac{\sum_{i=0}^m \sum_{j=0}^l (d_{i+1} - d_i) T_{ij}}{l \sum_{i=0}^m (d_{i+1} - d_i)}$$

where l and m represent the number of depths and the number of times, respectively, that readings were made, i and j represent a single time and single depth,

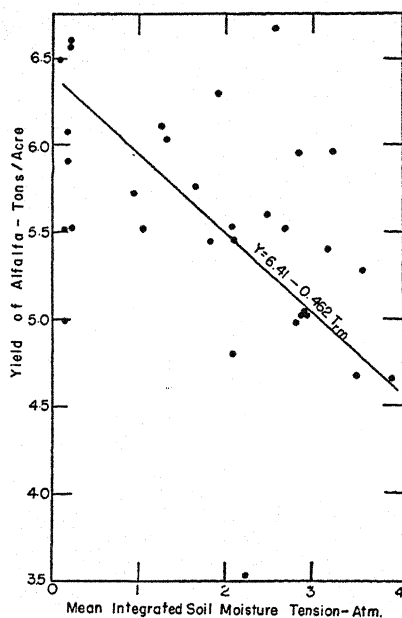


FIG. 2

FIG. 2. RELATIONSHIP OF MEAN INTEGRATED SOIL MOISTURE TENSION AND TOTAL YIELD OF ALFALFA

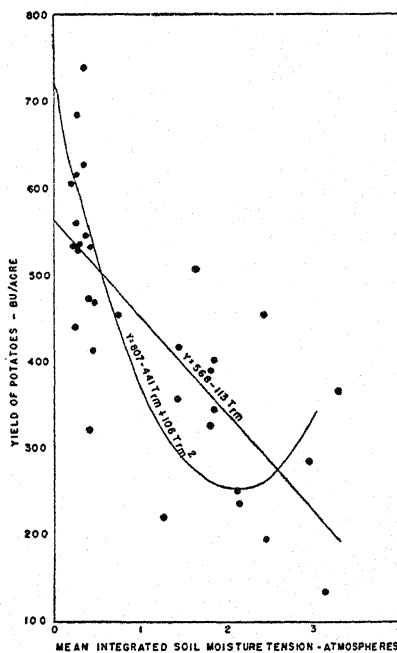


FIG. 3

FIG. 3. RELATIONSHIP OF MEAN INTEGRATED SOIL MOISTURE TENSION AND YIELD OF POTATOES

T_{ij} is the moisture tension at a single time and a single depth, and d_i represents the day of the year that observation i was made. The weighting factor that represents the time interval in days between successive readings is $(d_{i+1} - d_i)$.

This calculation was simply done with punch card machines by first multiplying each observed tension by the weighting factor then adding all the products for the several depths at one location that represented a single time. The results for the various times were then added to give a total or integrated tension, which was then divided by the product of the number of depths (l) by the sums of the weighting factor $(d_{i+1} - d_i)$.

The calculation of mean soil moisture tension for high tension sugar beet plot 114 is shown in table 2. The observed tension for each of the nine depths on the day of the year indicated has been multiplied by the weighting factor in column 2 then added to give the total in column 3. For example, the value in column 3 for day 261 is 213.6 atmospheres. This is obtained either by multiplying each of the tension readings for plot 114 given in table 1 by the weighting factor 6 or by multiplying the total for plot 114, which is 356, by the weighting factor 6. All other values in column 3 of table 2 were obtained in a like manner. The total weighted tension, 2731.7 atmospheres, was then divided by the total

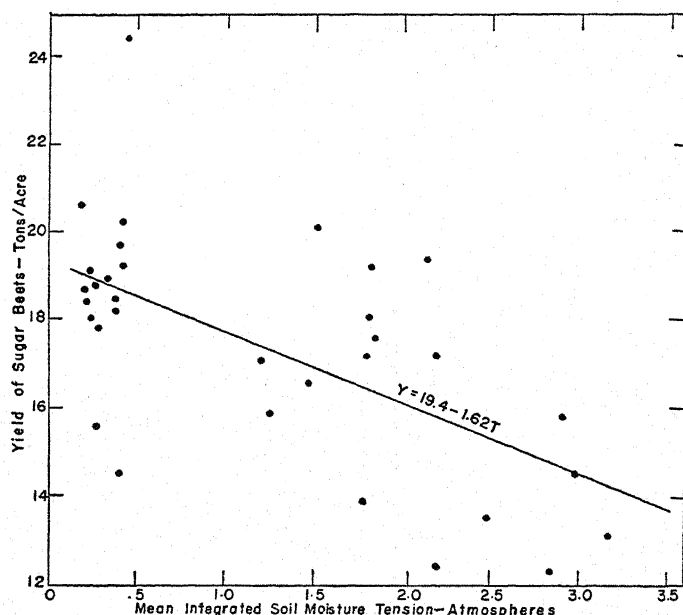


FIG. 4. RELATIONSHIP OF MEAN INTEGRATED SOIL MOISTURE TENSION AND YIELD OF SUGAR BEETS

number of observations represented, which is the product of the number of depths by the sum of the weighting factors, in this case

$$\frac{2731.7}{9 \times 113} = 2.69 \text{ atmospheres, or}$$

the mean integrated soil moisture tension for plot 114.

This same procedure was used for calculating the mean integrated soil moisture tension for all other plots of sugar beets, potatoes, and alfalfa.

EFFECT OF MEAN INTEGRATED SOIL MOISTURE TENSION ON YIELD

The regression of yields of established stands of alfalfa, potatoes, and sugar beets is shown in figures 2, 3, and 4. Since first year alfalfa received uniform moisture treatments to establish the stand, no yield data were taken. Despite

all other factors affecting the growth of these crops, the linear decrease in yield with increasing soil moisture tension is highly significant. Even though there is considerable divergence from regression, the high yields are mostly associated with low moisture tension values, and the low yields with high moisture tension values.

The significant curvilinear effect of integrated soil moisture tension on yields of potatoes results largely from the exceedingly rapid decrease of yields as mean integrated moisture tension increases from about 0.4 to 1 atmosphere.

The data indicate that under the conditions of this experiment an increase of 1 atmosphere mean integrated soil moisture tension within the range 0.4 atmosphere to 4 atmospheres will, 95 per cent of the time, reduce the yield of established stands of alfalfa between 0.65 and 0.27 tons per acre per year, and sugar beet yields will be reduced from 0.78 to 2.45 tons per acre per year. Since there was a significant deviation from linearity for potato data, the lowest yields of potatoes probably were attained sometime before soil moisture reached the permanent wilting percentage. The results also indicate that potatoes respond favorably to high moisture content in the soil as long as the soil is well drained and aerated.

The mean integrated soil moisture tension as calculated gives the average moisture content throughout the soil profile during the growing season. As soon as a moisture plot dried out to the point where irrigation was indicated, water was applied to wet the entire profile. Sufficient moisture at low tensions was available to the plant, therefore, for much of the time. The growth rate of the plant must, therefore, have been seriously reduced as moisture tension became high. Since the maximum moisture tension reached at any time on any of the plots was less than permanent wilting, it must be concluded that under the conditions of this experiment, moisture availability to plants for growth was decreased as moisture tension increased. The commonly accepted hypothesis that moisture is equally available to plants for growth throughout the entire plant growth range from field capacity to permanent wilting percentage is therefore untenable.

SUMMARY

The newly developed technique for measuring integrated soil moisture tension has been applied to crops grown in a rotation under different moisture conditions. The results of one year's experimentation is reported to illustrate the utility of the method. Depth of rooting of the crop is determined, the moisture tension integrated for depth is used as a criterion for irrigation, and the original data are shown to indicate the adequacy of irrigation application.

A single value representing the seasonal soil moisture regime, the mean soil moisture tension, has been related to yields of alfalfa, sugar beets, and potatoes showing that over the entire plant growth range of soil moisture, the yield is reduced as mean tension increases. This makes untenable the hypothesis that moisture is equally available to plants for growth throughout the entire plant growth range from field capacity to permanent wilting percentage.

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EFFECT OF CERTAIN CATIONS AND ANIONS ON PHOSPHORUS AVAILABILITY

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Received for publication November 5, 1951

The reactions taking place when phosphate fertilizers are added to calcareous, saline, saline-alkaline, and alkali soils of the western United States are of importance in determining the fertilizer practices of these areas. The problem is complicated by the wide variation in the types and proportions of the different native salt constituents. In general, it has been found that neutral salts such as CaSO_4 and CaCl_2 , which have a common ion with the phosphate compound, tend to decrease the solubility of P_2O_5 (5, 15).

Buehrer (5), McGeorge and Breazeale (13), and others (1, 6, 7, 14) have studied fixation of P_2O_5 in calcareous soils. These workers agree, for the most part, that certain compounds are formed in the reaction between CaCO_3 and the P_2O_5 added as fertilizer. Bassett (2), Breazeale and McGeorge, and Buehrer have suggested that a carbonate apatite or hydroxyapatite is the end product of this reaction. The formation of a dicalcium and a tricalcium phosphate has been postulated from a study of the $\text{H}_2\text{O}-\text{CO}_2-\text{CaO}-\text{P}_2\text{O}_5$ system by Cameron and Bell (9), Cameron and Hurst (8), Bassett (2) and Britton (4). Buehrer concluded that the solubility equilibrium of this system is determined not by tricalcium phosphate but by dicalcium or monocalcium phosphate which is present on the surface of tricalcium phosphate crystals as a result of hydrolytic action.

Boischot *et al.* (3), working with calcareous sands, found that the quantity of P_2O_5 fixed is a function of particle size. The number of CaCO_3 crystals is directly proportional to the surface area of these crystals.

Literature describing the effect of neutral salts having no common ion on P_2O_5 availability is conflicting. Some investigators have found that certain salts increase availability, whereas others find the opposite to be true. Buehrer (5) reported that, in general, neutral salts having no common ion increase the solubility of the slightly soluble P_2O_5 salt.

The purpose of this study was to investigate the influence of the carbonates, sulfates, and chlorides of calcium, magnesium, and sodium on, first, the availability of fertilizer P_2O_5 and, second, the availability of soil P_2O_5 .

MATERIALS AND METHODS

The soil selected for this study was obtained from the university field station at Lewiston, Idaho, and showed the following analysis: pH, 7.2; total soluble salts, 700 ppm.; inorganic carbonates, 0.06 per cent; available P_2O_5 , 65 ppm.;² cation-exchange capacity, 18.2 me./100 gm.

¹ From a study conducted as part of a regional phosphorus program; Idaho Agricultural Experiment Station Research Paper 342.

² Available P_2O_5 was determined by the CO_2 extraction method (10).

The soil was air-dried and screened through a 2-mm. sieve. Twenty-one pounds was weighed into each of 36 steel cylinders, 15 inches long by 8 inches outside diameter. The cylinders had been coated with Biturine paint. Three levels of the following salts were added, with each level of salt treatment applied to a different cylinder: CaCO_3 , CaSO_4 , CaCl_2 —2, 4, 8 per cent by weight of soil; MgCO_3 , MgSO_4 , MgCl_2 —1, 2, 4 per cent by weight of soil; Na_2CO_3 , Na_2SO_4 , NaCl —0.1, 0.2, 0.4 per cent by weight of soil. Nine cylinders of soil reserved for check treatments received no salt additions. The soil in the cylinders was made up to field capacity with distilled water and allowed to incubate for a month. At the end of this period, superphosphate tagged with P32 was thoroughly mixed into each cylinder of soil including the check cylinders.³ The fertilizer was added at the rate of 100 pounds of available P_2O_5 per acre. The activity of the fertilizer at the time of application was about 0.2 millicurie per gram of P_2O_5 . The soil in each cylinder was then divided into five smaller pots to provide five replications for each level and salt treatment. The 180 pots in the experiment were covered to minimize evaporation and randomized on large tables.

Two weeks after the fertilizer application, the soil in each pot was sampled, air-dried, and sieved. Available phosphorus was determined by the CO_2 extraction method (10). Fertilizer phosphorus in the extract from the latter procedure was determined by an RCL Mark 1 solution counter and thence from the calculation:

$$\frac{\text{Specific activity of extract}}{\text{Specific activity of fertilizer}} \times 100.$$

The separation of available fertilizer and soil phosphorus may not be an absolute measure in view of isotopic exchange of P32 for P31 on the interfaces of the soil colloids (12). It was not the purpose of this investigation to establish absolute values in phosphorus fixation as affected by various salts and concentrations, but rather to obtain relative values. For this reason, only one method of estimating available phosphorus was used.

RESULTS AND DISCUSSION

Fertilizer P_2O_5

The effect of the various salts on the availability of P_2O_5 from the fertilizer applied to the soil, and hereafter referred to as "available fertilizer P_2O_5 ," is shown in table 1. In this table the check treatment refers to soil receiving fertilizer without any additional salt treatment. In the presence of Ca^{++} , the Cl^- gave the greatest availability of P_2O_5 .⁴ There was no difference between the effect of CO_3^{--} and SO_4^{--} in the presence of Ca^{++} . In the presence of Mg^{++} , the CO_3^{--} gave the greatest availability, and Cl^- the least. In the presence of Na^+ , the CO_3^{--} gave the greatest availability and SO_4^{--} the least. The effect

³ Radioactive superphosphate was furnished by the U. S. Department of Agriculture, Beltsville, Md.

⁴ C. I. Seely kindly aided in the statistical interpretation of the data.

of the SO_4 anion was sufficient at the medium and high rates to eliminate the effect of Na^+ and to result in a decrease in availability of fertilizer P_2O_5 below that of the check.

TABLE 1

Effect of various cations and anions applied at different rates on availability of fertilizer P_2O_5 , ppm. of fertilizer P_2O_5

CHECKS*	15.69	14.11	15.33	14.27	13.95	15.42	13.13	13.96	14.27
RATES	CaCO_3	CaSO_4	CaCl_2	MgCO_3	MgSO_4	MgCl_2	Na_2CO_3	Na_2SO_4	NaCl
Low.....	9.28	8.38	11.47	13.44	12.53	10.64	18.65	16.83	16.31
Medium.....	7.02	7.69	10.19	11.69	11.55	12.53	19.26	11.77	18.47
High.....	8.00	8.00	5.97	14.32	14.11	10.64	16.33	11.02	15.85

L.S.D. at 1 per cent level, 3.59.

* Tagged P_2O_5 added; no salts added to this treatment.

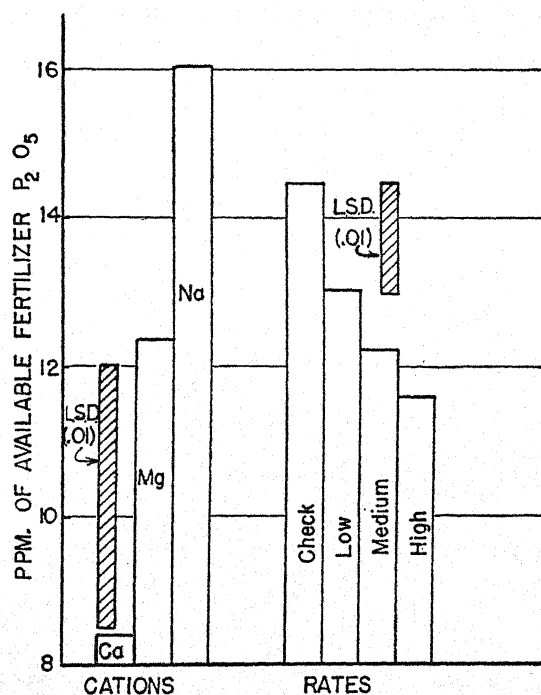


FIG. 1. EFFECT OF CATIONS AND RATES OF APPLICATION ON AVAILABILITY OF FERTILIZER P_2O_5

The effect of the cations Ca^{++} , Mg^{++} , and Na^+ on the availability of fertilizer P_2O_5 is shown in figure 1. These results represent the over-all averages of the three respective cations, and the differences in their effects are highly significant. The influence of the three anions CO_3 , SO_4 , and Cl on availability appeared to be masked by the cation effect; the means for the anion values are

not presented. The figure shows the depressant action of Ca^{++} on the availability of fertilizer P_2O_5 and the greatly enhanced availability due to Na^+ .

TABLE 2

Effect of various cations and anions applied at different rates on availability of soil P_2O_5 ppm. of soil P_2O_5

CHECKS*.....	85	82	82	81	82	82	77	87	85
RATES	CaCO_3	CaSO_4	CaCl_2	MgCO_3	MgSO_4	MgCl_2	Na_2CO_3	Na_2SO_4	NaCl
Low.....	66	73	64	59	71	68	94	92	87
Medium...	61	60	48	82	83	47	101	85	90
High.....	37	51	47	74	100	50	125	56	75

L.S.D. at 1 per cent level, 25.

* Tagged P_2O_5 added; no salts added to this treatment.

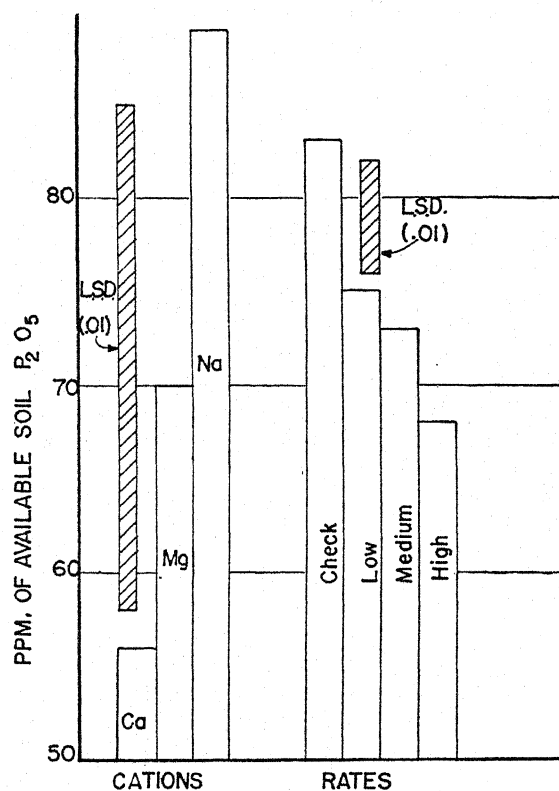


FIG. 2. EFFECT OF CATIONS AND RATES OF APPLICATION ON AVAILABILITY OF SOIL P_2O_5

Figure 1 also illustrates the effect of rate of salt treatment on the availability of fertilizer P_2O_5 . The soil was treated with the various salts to simulate salt conditions found in southern Idaho soils. For this reason, the differences in rates between different salts are not comparable on a percentage or on a molar

basis. The rate bars, however, represent over-all averages for all salts at the four different rates of treatment. The data show that increasing the rate of application of the Ca, Mg, and Na salts causes a general decrease in the availability of fertilizer P_2O_5 .

Soil P_2O_5

The effect of the various salts on the availability of P_2O_5 in the soil other than that added by the fertilizer is shown in table 2. This fraction, hereafter referred to as "available soil P_2O_5 ," was determined by subtracting the fertilizer P_2O_5 fraction from the total available P_2O_5 . The effect of the salt treatments on the availability of fertilizer P_2O_5 and soil P_2O_5 is similar in direction although somewhat different in degree. For example, the depressant effect of Ca^{++} is not significantly different from the effect of Mg^{++} on availability of soil P_2O_5 , as shown in figure 2. Further, the effect of Na^+ on availability of soil P_2O_5 is not significantly greater than the effect of Mg^{++} . Both these differences are highly significant in figure 1. The effect of the anions on availability of soil P_2O_5 is very similar to the effect on fertilizer P_2O_5 . The only difference is that in the presence of Ca^{++} the SO_4^{--} gave the greatest availability of soil P_2O_5 .

The amounts of soil P_2O_5 made available in the check treatments range from 77 to 87 ppm. The available P_2O_5 in this soil was determined in the untreated soil to be 65 ppm. (table 2). Several workers have reported increased uptake of soil P_2O_5 by plants grown on phosphate-fertilized plots. Jordan *et al.* (11) found that potato tubers grown on phosphated plots took up more soil P_2O_5 than did tubers grown on untreated plots. Spinks and Barber (16), working with wheat, and Strzemienski (17), working with rye grass, reported similar occurrences. The data in table 2 indicate that the superphosphate treatment resulted in more soil P_2O_5 in the available state, except where certain salt treatments depressed the availability below the 65-ppm. level.

SUMMARY

In general, the salts of Ca, which have a common ion with the P_2O_5 fertilizer compound, caused the greatest fixation of both fertilizer and soil P_2O_5 . Sodium salts increased the availability of both fertilizer and soil P_2O_5 . Magnesium salts were intermediate between Ca and Na in their release of soil P_2O_5 and fixation of fertilizer P_2O_5 .

The anions Cl^- , SO_4^{--} , and CO_3^{--} varied in their effects on availability of soil and fertilizer P_2O_5 .

In general, increasing the rate of salts decreased the availability of fertilizer and soil P_2O_5 . Increasing the rate of Na_2CO_3 , however, increased both available soil and fertilizer P_2O_5 .

Phosphate fertilization increased the availability of soil P_2O_5 .

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ROLE OF SOLVATED SILICA IN PROMOTING MIGRATIONS OF FLUORINE, PHOSPHORUS, AND CALCIUM IN 10-YEAR RAIN-WATER DRAINAGE FROM SLAGGED AND WOLLASTONITED SOILS

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Received for publication November 9, 1951

Solvated silica functions as a weak acid in aqueous systems and can be titrated stoichiometrically (18). Even in its solid phase, finely ground, moist silicic acid will induce measurable evolution of CO_2 from its prolonged mixtures with CaCO_3 at 30°C . (3), and incorporations of precipitated silica served to correct the toxicity that 4-ton-per-acre inputs of MgO had induced on tobacco cultures in silt loams (4).

The quenched glassy slag from the electric rock phosphate-reduction furnace is comprised chiefly of calcium metasilicate, which undergoes hydrolytic disintegration readily after the slag is incorporated into the soil, where its component silica is liberated into hydrated state. This phenomenon is evidenced by the increases in the quantities of solvated silica and $\text{Ca}(\text{HCO}_3)_2$ that the rain-water drainage carries from slagged soils. Such increases are consonant with the liberations of silica that ensue from suspensions of wollastonite and of Wilson Dam slag in CO_2 -impregnated water with development of $\text{Ca}(\text{HCO}_3)_2$ concentrations far greater than those that develop in corresponding suspensions of CaCO_3 of various forms (11).

Then, too, extractions of the electric furnace slag in CO_2 -impregnated water gave concentrations of fluorides that were far greater than those obtained through corresponding extractions of fluorspar. The several laboratory extractions and pot culture studies prompted a 10-year lysimeter experiment upon the postulation that the rain-water drainages from slagged soils would carry a high concentration of fluorine as calcium silicofluoride.

The primary objectives of the present paper are to clarify that postulation and determine whether the slag-derived solvated silica would cause continued enhancements in the migrations of fluorine and calcium, and possibly PO_4 , into the rain-water leachings from slagged soils.

SOLVATED SILICA OUTGO

Solvated silica outgo from the untreated acidic soils was so meager that it was not determined quantitatively. Its occurrence in the rain-water leachings, as given in table 4, is differentiated from the suspensoid silicates that sometimes

¹ This experiment was conducted through cooperation between the chemistry department of The University of Tennessee Agricultural Experiment Station and the Divisions of Chemical Engineering and Agricultural Relations of Tennessee Valley Authority. Acknowledgment is accorded John Thompson and George Palmer, both formerly of T. V. A. personnel, for the analytical findings obtained in the first 4 years of the experiment.

appear in the drainage, after electrolyte solutes are washed from acidic soils by late fall and early winter rains. When the clear drainages from the Ca-saturated soils are evaporated, their contents of solvated silica are rendered crystalline.

The quantities of solvated silica in the leachings from the two limestoned soils were analytically identical and were approximately only a fifth of the mean of the quantities leached from the slag and from the wollastonite. The solvated silica outgo induced by each liming material in the Hartsells soil was respectively comparable to the corresponding outgo from the Baxter soil.

A leaching of 165 pounds of silicon (Si), would meet the CaSiF_6 requirement for the 672.8-pound enhancement in the total outgo of fluorine from the slagged Hartsells soil. But that enhancement was accompanied by a *silicon* outgo of 513 pounds, which was more than three times the quantity essential to account for the fluorine's having been leached as silicofluoride. Similar relationship prevailed in the 10-year leachings from Baxter silt loam.

With identical input of calcium, as slag and as wollastonite, the outgo of silica from the wollastonite in each soil was somewhat beyond the outgo of SiO_2 from the corresponding input of slag, the silica content of which was not attributable entirely to occurrence of Ca-metasilicate. If the 1,100-pound 10-year outgo of SiO_2 is credited to having come entirely from the incorporated wollastonite, the quantity of silica leached from it was only 0.048 per cent of its total content of silica. But the leaching of that quantity of silica leaves the wollastonite largely as such, as emphasized by the small accumulation of CaCO_3 in the wollastonited soil, in contrast to the large accumulations of CaCO_3 from the incorporated slag.

EXPERIMENTAL

Limestone and wollastonite, the metasilicate of calcium, were utilized as controls in comparisons with the quenched Wilson Dam slag. The three materials were passed through 100-mesh sieves and were incorporated simultaneously into Hartsells fine sandy loam, pH 5.0, and into Baxter silt loam, pH 5.2. Each material was mixed throughout 100-pound portions of soil, moisture-free basis, in a quantity equivalent to 20-tons of CaCO_3 per 2,000,000 pounds of soil, in asphaltum-coated galvanized iron lysimeters of 1/20,000 acre. Through pot cultures, in which the three liming materials had been incorporated at ranges of 2 tons to 20 tons per acre and in three degrees of fineness, it had been learned that the unground 10-mesh slag and 100-mesh wollastonite could be used at 20-ton rate without the decidedly toxic effect that was an early and transient result from the inputs of the slag that had been ground to pass 100-mesh (10). In the present experiment, the three materials used were finer than 100-mesh to assure uniformity in particle size. The 20-ton rate for the incorporations was adopted with expectancy that the extent of variations in effects would be registered significantly through analyses of the soils and their rain-water leachings.

The quenched slag had an 84.1 per cent CaCO_3 -equivalence (19) and contained 50 per cent CaO and 42 per cent SiO_2 . It contained 3.2 per cent of fluorine

and 1.3 per cent of P_2O_5 (10). Composition, reactive properties, and liming and fertilizer effectiveness of the slag, quenched and unquenched, have been described (6, 8, 9, 10, 13). The limestone had a $CaCO_3$ -equivalence of 99.5 per cent and contained only 1 per cent of $MgCO_3$. The crystalline wollastonite was equivalent to 82 per cent $CaCO_3$ and contained 1 per cent $CaCO_3$. The limestone and the wollastonite contained mere traces of fluorine and P_2O_5 .

Analytical procedures—other than those used to determine contents of fluorine and phosphorus in the drainage waters and sulfide sulfur in the slag (20)—were those prescribed in A.O.A.C. methods (1). The quantities of fluorine native to the Hartsells and Baxter soils were found to be 200 ppm. and 160 ppm., respectively, by the direct $H_2SO_4-HClO_4$ distillation technique (16). The Sanchis

TABLE 1

Ionic increments carried by the annual composites of the periodic collections of rain waters obtained at the Knoxville lysimeters, 1940-1950

ANNUAL PERIOD	RAIN WATERS	pH	COMPONENTS BROUGHT TO SOIL PER ACRE					
			Ca*	Mg*	S	K	P	N
	<i>inches</i>		<i>lb.</i>	<i>lb.</i>	<i>lb.</i>	<i>lb.</i>	<i>lb.</i>	<i>lb.</i>
1940-41	35.80	—	95	22	53	9	—	—
1941-42	41.20	—	93	25	65	12	—	—
1942-43	57.88	7.4	130	25	47	7	0.1	8
1943-44	51.19	7.1	115	19	40	9	0.2	7
1944-45	55.60	7.1	108	19	50	9	0.1	6
1945-46	53.81	6.9	123	22	57	6	0.1	6
1946-47	50.98	7.7	138	25	53	7	0.1	2
1947-48	42.69	6.7	98	31	77	16	0.3	6
1948-49	56.57	7.0	90	38	52	15	0.8	9
1949-50	62.60	6.7	100	31	31	14	0.6	4
10-year total	508.32		1090	257	525	104	2.3†	48‡
Average annual	50.83		109	26	53	10	0.3	6

* Expressed as $CaCO_3$ -equivalence.

† For 8 years; computed to 2.9 pounds for 10 years.

‡ For 8 years; computed to 60 pounds for 10 years.

procedure (17) was used for determination of fluorine carried by the drainage waters, and their phosphorus contents were determined by means of a modification of the A.O.A.C. microchemical method (22).

Increments brought to the soils by the rain waters are recorded in table 1 and the data of tables 2 and 7 give the initial and final properties and pH values of the two soils.

FLUORINE MIGRATIONS

The occurrence of fluorine in the 10 annual composites of the periodically collected leachings from the two soils are given in table 3.

Total passages of fluorine were increased slightly by the limestone and by the wollastonite, although both of the materials were almost devoid of fluorine.

The mean difference between the per annum passages of fluorine from the limestone and the wollastonite in each soil was less than a pound per acre and this difference is not sufficient to prove that the silica content of the incorporated wollastonite caused an increase in the outgo of fluorine from supplies that were natural to the soils. In a related 10-year experiment, however, the mean of the leachings from the triplicated cumulative inputs of 4,932 pounds of CaF_2 per acre registered only 4.5 pounds of fluorine as outgo per acre per annum (15). That outgo represented only a small fraction of the stoichiometric equivalence of the calcium enhancement in the leachings from the incorporated CaF_2 . Obviously, increases in the migrations of fluorine—68 pounds and 63 pounds per annum—from the heavily slagged Hartsells and Baxter soils, were in association with calcium in form or forms far more dissoluble than the simple fluoride.

TABLE 2

Exchangeable bases in Hartsells fine sandy loam and in Baxter silt loam controls, before and after 10 years' leachings by rain waters*

BASE	HARTSELLS FINE SANDY LOAM† EXCHANGEABLE BASIS		BAXTER SILT LOAM‡ EXCHANGEABLE BASIS	
	Initial	Final	Initial	Final
	me.	me.	me.	me.
Calcium.....	1.68	0.88	1.48	1.10
Magnesium.....	0.25	0.15	0.36	0.19
Potassium.....	0.13	0.09	0.14	0.09
Hydrogen§.....	4.39	3.91	3.97	3.70
Exchange capacity¶.....	6.45	5.03	5.95	5.08
CO_2	0.0	0.0	0.0	0.0

* As millequivalents per 100 gm. of dry soil.

† Initial pH was 5.0.

‡ Initial pH was 5.2.

§ Represents difference between the sum of Ca, Mg, and K and exchange capacity.

¶ Obtained by means of ammonium acetate extraction at pH 7.0.

The x-ray examination of the slag did not register incidence of CaF_2 in the slag or in a mixture of no-pattern material into which a 6.7 per cent content of CaF_2 had been mixed to simulate a slag of such fluoride content.

Upon the assumption that the fluorine content of the electric furnace slag occurs in solid solution of the large proportion of the metasilicate of calcium, the following equations indicate the transitions that ensue after the slag is incorporated into soil:

- $\text{CaSiO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{SiO}_2$
 - $\text{Ca}(\text{OH})_2 + \text{H}_2 \text{ of complex} \rightarrow \text{Ca complex} + 2\text{H}_2\text{O}$
 - $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
 - $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaH}_2(\text{CO}_3)_2 \rightarrow \text{into the rain-water drainage.}$
- Solid $\text{CaSiF}_6 + n\text{H}_2\text{O} \rightarrow \text{solute CaSiF}_6 \rightarrow \text{into the rain-water drainage.}$

The Ca of the engendered hydroxide replaces the hydrogen of the soil acidoids, and the Ca in excess of that requirement undergoes conversion to CaCO_3 in

solid phase and into a bicarbonate solution that stabilizes the concomitant calcium silicofluoride and promotes its migration, as in table 6.

As noted, the enhancements in calcium outgo from incorporations of CaF_2 in related experiments were substantially greater than the relatively small parallel increases in the outgo of the associated fluorine (14). Obviously, most of the fluorine of the incorporated calcium fluoride underwent fixation by the aluminous complexes of the soil systems. In contrast, the fluorine of the slag underwent extensive leaching from the soil instead of becoming fixed by it. Because the fluorine of additive CaF_2 was retained so largely by the soil, the substantial

TABLE 3

Fluorine outgo in 10-year rain-water leachings from 20-ton CaCO_3 -equivalent incorporations of 100-mesh limestone, slag, wollastonite in two soils*

YEAR	FLUORINE PER 2,000,000 POUNDS OF SOIL†							
	From Hartsells Fine Sandy Loam and‡				From Baxter Silt Loam and§			
	Alone	Limestone	Slag	Wollastonite	Alone	Limestone	Slag	Wollastonite
	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.
1	0.2	0.5	42.4	0.5	0.2	0.3	40.5	0.5
2	0.4	0.8	93.6	1.2	0.3	0.7	71.6	1.0
3	0.4	0.9	94.1	1.6	0.4	1.3	72.3	2.1
4	1.0	1.6	75.8	2.2	0.7	0.9	80.1	1.3
5	2.6	4.3	114.3	7.5	2.9	7.4	103.3	4.2
6	2.4	3.4	64.8	5.8	2.4	2.3	57.9	3.3
7	1.0	2.7	47.4	2.8	1.9	2.5	48.1	3.3
8	0.8	2.3	33.7	2.3	0.9	2.2	25.5	2.4
9	3.5	3.6	59.0	5.8	2.6	1.2	61.0	3.5
10	1.4	4.2	61.4	4.2	1.4	2.7	57.1	4.2
Total Induced increase	13.7	24.3 10.6	686.5 672.8	33.9 20.2	13.7 —	21.5 7.8	617.4 613.7	25.8 12.1

* Made into full depth of soil, which then was undisturbed 10 years.

† Moisture-free basis.

‡ Fluorine content was 184 ppm.

§ Fluorine content was 200 ppm.

increase in the outgo of both fluorine and calcium in the drainage waters from the slagged soils is attributed to the migration of the relatively soluble silicofluoride, as in equation 2. The relationships of total migrations of fluorine to those of silica are obvious from a comparison of the totals in tables 3 and 4.

Apparently, the invariable enhancements in the silica outgo from the slagged soils were not governed by companion migrations of fluorine. Although the data indicate that the solvated silica in the leachings from the slagged soils did promote the outgo of the fluorine, paucity of native supplies of fluorine in the soils did not diminish the leachings of solvated silica from the incorporated wollastonite. Both of the distinctive calcium metasilicate materials imparted significant quantities of solvated silica to the drainages from both soils, and

the evolution of solvated silica in the silicate-enriched soil systems did increase the leaching of fluorine, even where none was incorporated.

TABLE 4

Silica outgo in 10-year rain-water leachings from 20-ton CaCO_3 -equivalent incorporations of 100-mesh limestone, slag, wollastonite in two soils*

YEAR	SiO ₂ PER 2,000,000 POUNDS OF SOIL†					
	From Hartsells Fine Sandy Loam and			From Baxter Silt Loam and		
	Limestone	Slag	Wollastonite	Limestone	Slag	Wollastonite
	lb.	lb.	lb.	lb.	lb.	lb.
1	1	97	39	4	69	25
2	24	67	112	17	49	116
3	13	118	121	13	102	134
4	10	109	93	7	88	93
5	10	140	125	1	125	118
6	9	121	110	1	110	103
7	14	90	102	10	94	91
8	25	59	81	94	115	146
9	39	167	212	16	99	150
10	73	132	175	55	150	206
Total	218	1100	1170	218	1001	1182
Increase from additive SiO ₂ ‡	—	882	952	—	783	964

* As in table 3.

† Moisture-free basis.

‡ That carried by the slag and by wollastonite.

PHOSPHORUS OUTGO

The limestone incorporations caused no increase in phosphate migration from the soils used in the present experiment. The same result obtained also in a related 10-year experiment from inputs of limestone, either alone or with CaF_2 (15). In the present experiment, however, the two metasilicate materials caused significant annual increases in the migrations of phosphates from both soils.

In general, the order of the increases in the leachings of phosphorus from the wollastonited Baxter soil was similar to the order induced by the slagged soil. Except for increments from the atmosphere, the quantities of phosphorus that passed from the wollastonited Hartsells and Baxter soils were from their respective native stores of 460 pounds and 620 pounds of P_2O_5 per 2,000,000 pounds of soil. Nevertheless, those passages were nearly equal to those of phosphorus from the two slagged soils that had been enriched through the 312-pound-per-acre input of phosphorus carried by the incorporated slag. Because of this comparison, and because the outgo of solvated silica from the wollastonited soils exceeded the corresponding outgo from the slagged soils, it appears that—within rational limits, and to the exclusion of soils of high apatite content—the passage of phosphorus into the drainage waters of soils well supplied with calcium is

influenced by the quantities of mobile silica in the soils, as well as by the percentage of the companion phosphate. Because of such mobilization of phosphorus into the drainage waters, it appears probable that phosphates will prove more effective on soils of good content of calcium and solvated silica. The total migrations of phosphorus from the several soil systems are shown in table 5.

TABLE 5

Phosphorus outgo in 10-year leachings from 20-ton CaCO_3 -equivalent incorporations of 100-mesh limestone, slag, wollastonite in two soils*

YEAR	PHOSPHORUS PER 2,000,000 POUNDS OF SOIL†															
	From Hartsells Fine Sandy Loam‡ and								From Baxter Silt Loam§ and							
	Alone		Limestone		Slag		Wollastonite		Alone		Limestone		Slag		Wollastonite	
	P	P ₂ O ₅	P	P ₂ O ₅	P	P ₂ O ₅	P	P ₂ O ₅	P	P ₂ O ₅	P	P ₂ O ₅	P	P ₂ O ₅	P	P ₂ O ₅
	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.
1	.11	0.25	.05	0.11	0.15	0.34	0.06	0.14	.04	0.09	.20	0.46	0.09	0.21	0.02	0.05
2	.05	0.11	.10	0.23	0.21	0.48	0.14	0.32	.05	0.11	.09	0.21	0.19	0.44	0.19	0.44
3	.11	0.25	.16	0.37	0.38	0.87	0.26	0.60	.06	0.14	.11	0.25	0.39	0.89	0.33	0.76
4	.05	0.11	.05	0.11	0.25	0.57	0.15	0.34	.06	0.14	.05	0.11	0.20	0.46	0.14	0.32
5	.12	0.27	.12	0.27	0.44	1.01	0.40	0.92	.13	0.30	.12	0.27	0.53	1.21	0.40	0.92
6	.17	0.39	.20	0.46	0.40	0.92	0.57	1.31	.04	0.09	.17	0.39	0.57	1.31	0.49	1.12
7	.11	0.25	.07	0.16	0.33	0.76	0.40	0.92	.05	0.11	.04	0.09	0.41	0.94	0.28	0.64
8	.06	0.14	.05	0.11	0.22	0.50	0.32	0.73	.05	0.11	.06	0.14	0.40	0.92	0.33	0.76
9	.15	0.34	.09	0.21	0.50	1.15	0.56	1.28	.06	0.14	.06	0.14	0.67	1.53	0.56	1.28
10	.06	0.14	.07	0.16	0.68	1.56	0.70	1.60	.06	0.14	.07	0.16	0.89	2.04	0.76	1.74
Total	.99	2.25	.96	2.19	3.56	8.16	3.56	8.16	.60	1.37	.97	2.22	4.34	9.95	3.50	8.03
Induced increase			—	—	2.57	5.91	2.57	5.91	—	—	.37	0.85	3.74	8.58	2.90	6.66

* As in table 3.

† Moisture-free basis.

‡ Phosphorus content was equivalent to 0.023 per cent P_2O_5 .

§ Phosphorus content was equivalent to 0.031 per cent P_2O_5 .

CALCIUM OUTGO AS BICARBONATE

The occurrences of $\text{Ca}(\text{HCO}_3)_2$ in the leachings from the two untreated soils and from the incorporations of slag, wollastonite, and limestone are shown in table 6 and comparatively with calcium totals in figure 1. The findings reported by Harris *et al.* (2) indicate that the bicarbonate leachings from the limestoned soil could have come from both the sorbed Ca and the undecomposed fraction of the incorporated limestone, whereas such leachings from the glassy slag and from the crystalline wollastonite were governed by the extent of the hydrolytic disintegrations of their metasilicate contents. Included also in the comparisons was the relationship that bicarbonate leachings bear to final occurrences of soil carbonates, as residues from the incorporated limestone and as cumulations engendered from the two silicate materials, as in table 7, in which are recorded

also the final pH values resultant from the incorporations of the three liming materials.

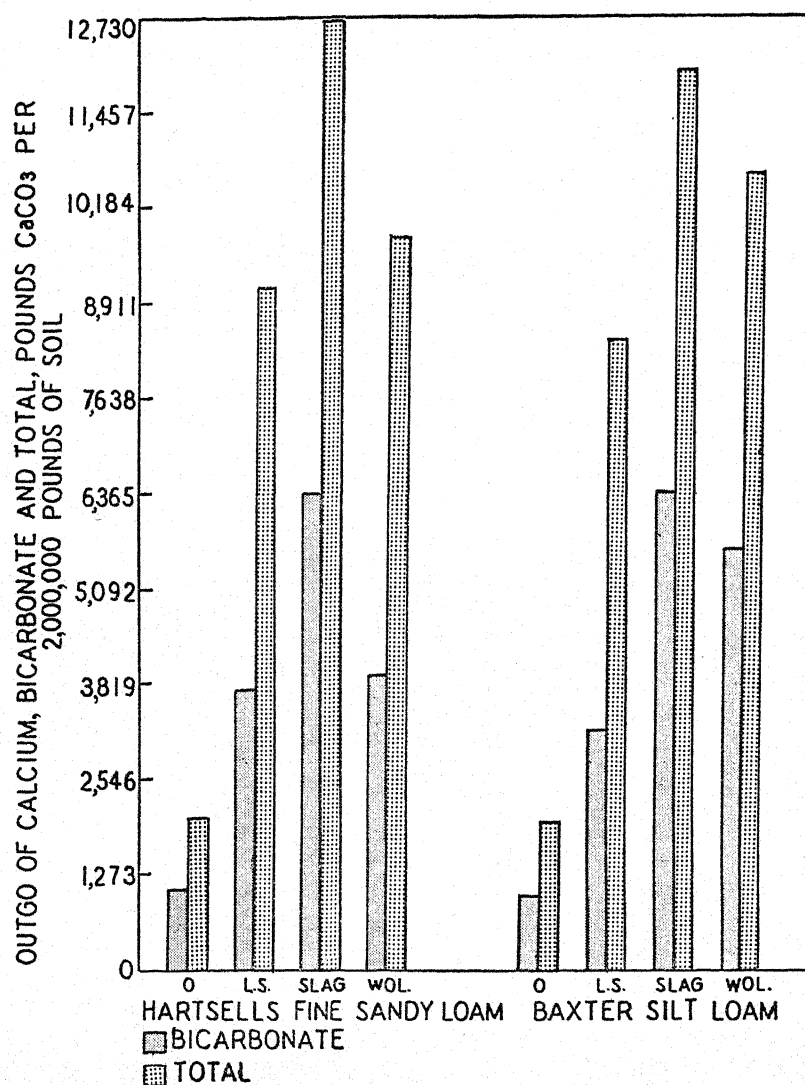


FIG. 1. INFLUENCE OF Ca-METASILICATE MATERIALS ON 10-YEAR LEACHINGS OF CALCIUM, AS BICARBONATE AND AS TOTALS, FROM HARTSELLS FINE SANDY LOAM AND BAXTER SILT LOAM AFTER SEPARATE INCORPORATIONS OF 100-MESH LIMESTONE, GLASSY SLAG, AND WOLLASTONITE, EACH IN QUANTITIES EQUIVALENT TO 20 TONS OF CaCO_3 PER 2,000,000 POUNDS OF SOIL (MOISTURE-FREE BASIS).

Every periodic collection of the *leachings* from each of the calcic materials in the 10 years of the experiment was found to be alkaline, in pH range from 7.7 to 8.2. The leachings of bicarbonate from the slagged Hartsells and Baxter

TABLE 6

Calcium bicarbonate outgo in 10-year rain-water leachings from 20-ton CaCO₃-equivalent incorporations of 100-mesh limestone, slag, wollastonite in two soils*

YEARS	Ca(HCO ₃) ₂ PER 2,000,000 POUNDS OF SOIL†							
	Hartsells Fine Sandy Loam and				Baxter Silt Loam and			
	None	Limestone	Slag	Wollastonite	None	Limestone	Slag	Wollastonite
	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.
1	53	210	438	254	39	135	501	247
2	98	510	964	624	80	435	847	775
3	81	478	917	537	72	524	884	765
4	79	479	950	526	91	416	912	770
5	169	535	824	516	160	465	750	713
6	113	516	755	470	106	474	691	640
7	91	524	563	392	90	356	676	496
8	88	368	505	346	85	302	452	587
9	132	527	724	491	129	459	650	637
10	169	673	793	741	150	609	960	989
Total	1073	4820	7433	4897	1002	4175	7323	6619
Increase	—	3747	6360	3824	—	3173	6321	5617
Increase as % of input of CaCO ₃ -equivalent		9.4	15.9	9.6		7.9	15.8	14.0

* As in table 3.

† Moisture-free basis.

TABLE 7

*Calcium carbonate occurrences in two soils after 10 years of rain-water leachings from 20-ton CaCO₃-equivalent incorporations of limestone, quenched calcium silicate slag, and wollastonite**

INCORPORATIONS FULL DEPTH	FINAL VALUES FOR HARTSELLS FINE SANDY LOAM			FINAL VALUES FOR BAXTER SILT LOAM		
	CaCO ₃		pH	CaCO ₃		pH
	me.	lb.*		me.	lb.*	
None.....	0	0	5.1†	0	0	5.4‡
Limestone.....	24.3	24,300	7.9	24.9	24,900	7.9
Slag.....	16.6	16,600	8.0	17.3	17,300	8.0
Wollastonite.....	0.7	700	7.8	1.1	1,100	8.1

* Per 2,000,000 pounds of soil.

† Initial value was 5.0.

‡ Initial value was 5.2.

soils were maximal and nearly identical, or 6,360 pounds and 6,321 pounds. Because every annual leaching of bicarbonate from the slagged soils exceeded the corresponding outgo from the limestoned soils, the accumulations of CaCO₃ from the slag in the Hartsells and Baxter soils were only two thirds of the 12-ton

per acre residues of limestone in those soils, as shown by the data of table 7. In contradistinction, the two soils acquired respective accumulations of only 700 pounds and 1,100 pounds of CaCO_3 from the wollastonite, even though the

TABLE 8

Ten-year outgo of Ca, Mg, K, S, and N in rain-water leachings from 20-ton CaCO_3 -equivalent incorporations of limestone, slag, wollastonite (100-mesh) in Hartsells fine sandy loam*

In pounds per 2,000,000 pounds soil†

INCORPORATIONS	ANNUAL OUTGO										Total
	1	2	3	4	5	6	7	8	9	10	
Calcium											
None.....	113	145	88	91	69	54	47	56	64	77	804
Limestone....	487	505	372	410	322	326	284	258	308	369	3641
Slag.....	510	740	631	690	506	473	332	307	432	470	5091
Wollastonite..	574	572	467	454	343	312	254	252	312	398	3938
Magnesium											
None.....	22	37	24	31	17	10	6	13	17	23	200
Limestone....	4	14	4	8	5	2	1	2	1	1	42
Slag.....	4	7	13	11	11	6	5	5	6	5	73
Wollastonite..	5	10	6	10	5	2	2	3	1	2	46
Potassium											
None.....	2.7	5.2	3.2	6.4	10.0	5.3	3.8	3.4	7.0	7.8	54.8
Limestone....	1.8	2.5	1.1	2.3	3.1	2.3	1.4	1.9	2.4	1.4	19.2
Slag.....	5.8	7.3	6.4	6.7	6.7	4.3	1.2	1.7	3.0	2.0	45.1
Wollastonite..	1.2	1.9	2.1	1.4	3.2	2.9	1.0	1.5	2.3	0.7	18.2
Sulfur											
None.....	16	65	55	61	66	48	47	52	61	62	533
Limestone....	75	86	65	76	57	56	51	65	65	61	657
Slag.....	86	88	60	93	71	58	45	60	69	62	692
Wollastonite..	87	82	72	80	67	52	50	67	71	59	687
Nitrogen											
None.....	85	92	26	64	16	11	8	19	17	17	355
Limestone....	220	146	56	79	27	36	20	25	26	29	664
Slag.....	144	117	25	75	26	34	11	6	18	26	482
Wollastonite..	251	146	46	79	35	39	27	24	30	25	702

* As in table 3.

† Moisture-free basis.

leachings of calcium, as bicarbonate and as totals, from the wollastonited soils exceeded the corresponding leachings from the limstoned soils. The enhancement in the bicarbonate outgo from each slagged soil accounted for close to 16 per cent of the input of calcium. The $\text{Ca}(\text{HCO}_3)_2$ leachings from the Hartsells

soil were 53, 58, and 50 per cent of the total passages of calcium from the CaCO_3 -equivalent inputs of limestone, slag, and wollastonite, respectively. The rela-

TABLE 9

Ten-year outgo of Ca, Mg, K, S, and N in rain-water leachings from 20-ton CaCO_3 -equivalent incorporations of 100-mesh limestone, slag, wollastonite in Baxter silt loam*
In pounds per 2,000,000 pounds soil†

INCORPORATIONS	ANNUAL OUTGO										Total
	1	2	3	4	5	6	7	8	9	10	
Calcium											
None.....	108	122	78	108	83	60	52	55	60	68	794
Limestone....	410	489	370	364	339	279	233	245	290	352	3371
Slag.....	559	644	492	616	485	424	377	302	401	520	4820
Wollastonite..	492	600	481	495	408	370	260	334	315	494	4249
Magnesium											
None.....	25	42	25	57	22	11	10	11	12	13	228
Limestone....	9	16	7	13	9	3	3	3	3	7	73
Slag.....	11	21	13	18	14	8	7	7	8	9	116
Wollastonite..	9	13	8	14	8	3	3	3	2	7	70
Potassium											
None.....	21.9	16.3	10.6	17.2	17.9	10.2	4.8	6.2	7.2	7.1	119.4
Limestone....	8.9	8.5	6.6	7.8	7.9	5.7	3.3	5.9	5.8	6.2	66.6
Slag.....	2.8	8.4	11.3	11.8	8.6	6.9	2.9	4.7	3.7	3.6	64.7
Wollastonite..	17.3	6.5	11.0	4.5	4.2	4.4	2.1	3.1	2.4	1.4	56.9
Sulfur											
None.....	7	49	50	76	84	57	52	59	65	64	563
Limestone....	64	91	54	82	78	53	55	69	65	67	678
Slag.....	123	82	45	89	78	56	52	66	67	63	721
Wollastonite..	82	84	60	82	72	58	41	66	49	60	654
Nitrogen											
None.....	79	105	43	55	22	20	13	11	12	10	370
Limestone....	194	133	55	65	30	21	23	31	30	32	614
Slag.....	150	118	34	61	37	23	14	16	20	21	494
Wollastonite..	216	126	55	57	31	24	8	16	16	22	571

* As in table 8.

† As in table 8.

tionships of bicarbonate outgo the total outgo of calcium, as in table 6, 8, and 9, are shown in figure 1.

The relatively small cumulation of CaCO_3 from the incorporated wollastonite might be deemed in contradiction to the phenomenon that was demonstrated in the several laboratory studies (3, 6, 8) through which it was shown that the

suspensions of calcium metasilicates undergo ready conversion to CaCO_3 in carbonated water and afford concentrations of bicarbonate several times those derived from like suspensions of various types of CaCO_3 (11). In the laboratory extractions, however, the proportions of water and CO_2 to solid CaCO_3 were decidedly different from the proportions that occurred or could occur in the soil systems of the lysimeters. The characteristic behavior of wollastonite in soils is that it (a) supplies adequacy of nutrient calcium to plant growth, (b) yields bicarbonate leaching beyond that from an equivalence of limestone, (c) causes only small build-up of CaCO_3 , even long after incorporation of 100-mesh material in the soil, and (d) proves more effective than limestone for soil liming, "with virtually no restriction as to rate" (10, p. 80), as has been demonstrated through pot cultures (12, 13).

OUTGO OF Ca, Mg, K, S, AND N

The quantities of the several concomitant ions carried by the annual composites of the periodic collections of the leachings are reported in tables 8 and 9 for the Hartsells and Baxter soils, respectively.

Calcium

In conformity with the leachings of bicarbonate, every total outgo of calcium per annum from the slagged Hartsells soil exceeded the corresponding outgo from the limed soil; and, after the initial year, total outgo of calcium per annum from the slagged soil always exceeded annual outgo from the wollastonited soil. The total outgo of Ca from the wollastonite in the Hartsells soil was somewhat larger than that from the limestone, the difference being due chiefly to the larger passages from the wollastonite in the first 5 years.

In every year, the total outgo of Ca from the slagged Baxter soil, and also that from the wollastonited soil, exceeded the corresponding annual passage from the limed soil. Total outgo of Ca from the slagged soil was 43 per cent greater than that from the limed soil.

Magnesium

In line with numerous lysimeter findings from this station and from the Virginia station (21), each of the three liming materials effected substantial repression in every annual leaching of magnesium from both soils. Explanation for this phenomenon "of reciprocal repression" was set forth in the report of those findings.

Question arises whether an accumulation of solvated silica in a dolomited soil would also enhance the migration of magnesium. It does not appear feasible to effect an increase in the occurrence of solvated silica in a system where the occurrence of exchangeable magnesium would exceed the occurrence of exchangeable calcium. Although the content of magnesium in the drainages of dolomited soils may exceed the content of calcium after the incorporated dolomite undergoes decomposition, the dolomite would not supply additive silica to the soil, nor would incorporations of the relatively inert magnesium silicate minerals impart a substantial input of solvated silica.

Potassium

In harmony with findings reported in 1930 and in 1938 (5, 7) the three liming materials exerted decidedly repressive effect upon the ready migration of potassium from Hartsells and Baxter soils. The repressions exerted in the Baxter soils represented a 52 per cent mean decrease in the outgo of K. The repressive effect upon outgo of potassium from the slagged Hartsells soil was offset somewhat in the early years of the experiment, because of the 90-pound content of potassium in the 20-ton CaCO_3 -equivalent incorporation of slag. Consequently, the direct repressions induced by the limestone and the wollastonite exceeded the diminished effect indicated for K repression induced by the slag.

Sulfur

Each of the three calcic materials caused a substantial increase in the total outgo of sulfur from both soils. Similar results have been found repeatedly as an early effect of incorporations of liming materials and the aeration incident to their inmixing. The larger outgo of sulfates from the slagged soil, particularly in the initial year, probably reflects the oxidation of the 138-pound content of sulfide sulfur that was carried by the incorporated electric furnace slag (20).

Nitrogen

All of the liming material also caused enhancements in total leachings of nitrogen from both soils, but the increases in the nitrate outgo from the slagged soils were not so large as those induced by the limestone and by the wollastonite. This difference in total outgo of nitrogen is attributable chiefly to the retardative effect from the causticity that developed early, because of the hydrolysis of the heavy-rate inputs of 100-mesh slag. Nevertheless, the first year leachings of nitrates from both of the slagged soils were close to twice the corresponding leachings of nitrates from the untreated soils. Moreover, in related pot culture experiments, the repressive effects exerted by the 20-ton incorporations of 100-mesh slag on the initial crop were succeeded by decided fertility after the heavily slagged soils had undergone aging (10). In contrast, 20-ton-per-acre incorporations of the 10-mesh slag and of 100-mesh wollastonite were beneficial to the initial crop and to succeeding crops. But, the question of advisable and admissible rates for incorporations of 100-mesh slag is merely academic, because electric furnace slag of such fineness is not produced. The calcium silicate slag is decrepitated into a 10-mesh product through quenching, instead of being ground, and the unground material can be incorporated without restriction as to rate, as has been demonstrated in the greenhouse and in practice. In the present experiment, however, the slag was ground to pass a 100-mesh sieve to assure comparable surface to the input-charges of the three carriers of calcium, and to accentuate the effects that were postulated as taking place after the two silicate materials undergo disintegrations in two distinctive soils.

SUMMARY

Glassy calcium silicate slag, crystalline wollastonite, and limestone were incorporated, in equivalent quantities and separately, into two distinctive soils

in a 10-year lysimeter experiment to determine whether passages of fluorine, calcium, and phosphorus into rain-water drainage are influenced by the development of solvated silica from those incorporations.

Every periodic collection of the leachings from each Ca-fortified soil system was alkaline, in pH range of 7.3 to 8.2, and all final soil pH values were in range of 7.9 to 8.1.

Enhancements in solvated silica outgo from the slagged soils were accompanied by substantial increases in migrations of fluorine and also of calcium as bicarbonate and as totals per annum.

The increases in outgo of solvated silica from wollastonite and from slag were accompanied by increases in outgo of PO_4 from both soils; but, because of low percentage content of phosphorus in the slag, the outgo of phosphate from it exceeded the outgo that the incorporated wollastonite induced from native supplies.

Passages of calcium, as bicarbonate and as totals, from the incorporations of slag and wollastonite were always far greater than those from the limestoned soils, in consonance with the decided higher concentrations of bicarbonate imparted by suspensions of the two silicate materials to carbonatated water.

Although outgo of calcium from the incorporated wollastonite exceeded outgo from the equivalent incorporations of limestone in both soils, the accumulations of calcium carbonate from the wollastonite were small in contrast to the large accumulations of CaCO_3 from the slag and the large residues of the limestone.

Each of the three liming materials induced decreases in the leachings of potassium and magnesium.

The three calcic materials induced a substantial increase in the outgo of sulfur and nitrogen; but the increase induced by the heavy-rate input of 100-mesh slag was less than the increases induced by the other two carriers of calcium, probably because of high alkalinity from the slag in the initial year of the experiment.

The findings are believed to warrant the conclusion that, when sufficient silica is brought into solvated form from additive calcium metasilicates in fallow soils of good content of calcium, the migrations of fluorine, phosphorus, and calcium solutes in rain-water drainages will be increased, whereas outgo of potassium and magnesium solutes will be decreased.

It is noted that the quenched slag used was ground to 100-mesh so that the three calcic materials would be of like fineness in the experimental comparison. But the slag sold is granulated, and not ground. It carries a relatively small fraction of 100-mesh material and can be used effectively for soil liming without restriction as to rational rate, as has been demonstrated through the pot cultures and through extensive use in practice.

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LESSONS FROM THE FIRST HALF CENTURY OF SOIL SURVEY: I. CLASSIFICATION OF SOILS

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Received for publication September 7, 1951

The National Cooperative Soil Survey in the United States is just beginning its second half century. The first organized surveys were made in four widely separated areas in 1899. Since then, soil surveys have been made in some 1,600 other counties and areas. At the meetings of the Soil Science Society of America in 1949, the development, applications, and future of the national soil survey were discussed in a general program commemorating the fiftieth anniversary (7, 10, 16). The beginning of the second half century seems a good time to review progress and errors that have been made. To that end, this paper offers a brief sketch of the development of soil classification; the second paper in the series outlines the evolution of field methods of soil surveys. An effort is also made to draw lessons of general application for future work.

EARLY CLASSIFICATION OF SOILS

It is easy to overlook the relatively recent origin of the present scheme of soil classification in the United States¹ and to forget the trials of the early scientists who initiated its development. The effort necessary to accumulate the data upon which our present scheme largely rests and the thought put into the classification are clear enough from careful review of the evolution of the scheme. This evolution can best be traced by following the development of the soil type and soil series, both old categories now familiar to many people in the United States. More time and thought have been given to the concepts of the soil type and soil series than to other categories in the present scheme.

Concept of the Soil Type

The units mapped in 1899 in the first soil surveys in the United States were called "soil types" (18). Study of the first few maps and reports, however, shows that the soil type of 1899 was comparable to a fairly broad soil association as defined in 1949. The soil type of 50 years ago included areas of soils with one or two properties in common. All soils of a given type within a county were alike in some conspicuous feature; they were all from the same parent material, all wet, all rocky, and the like. Names given to some soil types in the first surveys were similar to those used for soil types now, for example, Suffield clay, but some of the mapping units were called "Connecticut Meadows," "Pecos conglomerate soil," and the like. The areas outlined on the maps and the descriptions in the reports indicate clearly that the first concept of the soil type

¹ The current approach in soil classification in the United States is summarized in *Soil Science*, vol. 67, no. 2, February, 1949.

was essentially a geographic one—bodies of soils with one or two features in common.

Concept of Soil Series

First mention of the soil series occurred about 1903 (17). By that time, field men had begun to see that the soils in widely separated areas were alike in several ways. They looked for a system of naming to show these relationships. Because the early soil scientists had taken their field methods from geology, the one science that had such methods, it was only natural for them to turn to that field for help. They chose the term "series" to cover geologically related soil types because that term had already been applied by geologists to a succession of beds of different textures in a sedimentary deposit. The place given to soil texture in this name reflects the widespread emphasis it received in the early investigations.

The concept of the soil series had become rather explicit by 1903. Instructions to field parties (17) for that year carry the following statements:

Much advance has been made in the past year in this matter of correlation and in using the names of soils to bring out their relations. Several of the original types have been merged into others, or have been given new names to bring them into a uniform series, where this could be done without danger of confusion. In doing this, the object has been to establish certain series in the different physiographic divisions of the United States, and we are finding that there are a few general classes of soils that are in a way related. Prominent among these are the Norfolk, Miami, Fresno, Cecil, and Hagerstown series. In each of these we have found or expect to find a stony loam, a gravel, gravelly loam, sand, fine sand, sandy loam, fine sandy loam, loam, silt, clay loam, and clay. . . .

When the Norfolk sand is being deposited the conditions somewhere in the area will undoubtedly be favorable to the deposition of gravel, of silt, of fine sand, of loam, and of clay, and wherever material of these characters is encountered, presumably coming from the same source and being deposited essentially at the same time, they should be given this distinctive name so as to show their relation to one another. Knowing as we do the processes of soil formation, either from the disintegration of rocks in place or the transportation by wind or water, we should expect that materials from the same source would differ in their texture. The relationship of the derived soils should be shown by the use of a common name. . . .

These statements indicate clearly, though indirectly, the prevailing concept of the soil series in 1903.

GRADUAL EVOLUTION OF THE CLASSIFICATION

With the addition of the series, the soil surveyors in 1903 had established two categories that are still recognized. The concepts of the soil type and series differ greatly from those of today. Furthermore, the concepts began to change soon after they were established. As they were tested in the mapping of soils, the concepts were found inadequate in certain ways. Changes were therefore made to accommodate them to observations of soils in the field.

The early development of the soil survey was discussed comprehensively by Coffey in 1911 (3). The following year he published a study of the soils of the United States in which proposed schemes of soil classification were carefully appraised and the requirements of a logical scheme clearly stated (4). In these

publications, attention was directed to the pioneer work done by the Russian scientists, and many of the later teachings of Marbut were foreshadowed. The ideas and approaches offered by Coffey received little attention 40 years ago.

From the present point in time and with the knowledge acquired since 1911, the approach advocated by Coffey seems clearly ahead of the state of knowledge of the soil science of his day. It is now clear that relatively too much attention was given to the geological nature of soil materials in the first 20 years of the soil survey. A proposal for a comprehensive scheme of classification offered in 1911 illustrates this emphasis (5). The proposed scheme consisted of five categories: type, series, group, province, and division. Soil types were to be defined in terms of texture and structure; soil series in terms of color, organic matter, drainage, and lime; soil groups according to source of the soil material (igneous rock, slate, etc.); soil provinces to mode of formation (residual, cumulose, ice-transported, etc.), and soil divisions to major mode of formation (sedimentary or transported). This proposal seems to have been an accurate reflection of prevailing concepts of soils and the general state of knowledge in soil science 40 years ago. Today the proposal is conspicuous for its lack of the concept of the soil profile.

In the development of soil classification in the United States, perhaps the biggest single change in approach occurred with the shift in emphasis to the soil profile about 30 years ago. This approach was first outlined by Marbut (8) in a historic paper before the Society for the Promotion of Agricultural Science in 1921. It was developed further in a paper presented in 1922 (9), from which the following statement is taken:

Returning now to the characteristics on which we must base a soil classification let us see what questions we ask of our soils. Soil characteristics have been referred to in this paper very often and they are doubtless abundant, but what are those of most importance and to which attention must be directed; you will recall that one of the fundamental propositions formulated above stated that all soils at maturity develop a soil profile, and that the features of the soil is expressed in the features of this profile

After listing ten properties of the profile, Marbut added:

All of you are familiar with the fact that the ultimate soil unit, the soil type, the species, includes all areas of soil having a uniform profile. . . .

In 1921, Marbut (8) also said:

It would be unsafe to predict that no other features, not now known, would ever become important as bases of differentiation. I am of the opinion that we have not yet discovered all the important features of the soils or all of the characteristics of soils worthy of consideration in soil definition and soil mapping.

The placing of emphasis upon the soil profile in the American soil survey represents a major change in approach, which followed by many years the introduction of the concept by Dokuchaev and other scientists in Russia (1). It is hard to overstate the significance to soil science of the concept of the soil profile. The effect on soil science, as others look back on its introduction, will be recognized as equal to that of the introduction of anatomy to biology some centuries

ago. In spite of its importance, the concept of the soil profile could be introduced into the American soil survey only after much field study. It was necessary that enough field observations be available to demonstrate convincingly that the old approaches left many questions unanswered. There were changes in approach in the American soil survey prior to 1921 and there have been further changes since that time. All of these changes are part of the evolutionary process that follows from the continued gathering and reappraisal of data. Among the many changes that have occurred, however, none is of more importance than the introduction of the concept of the soil profile.

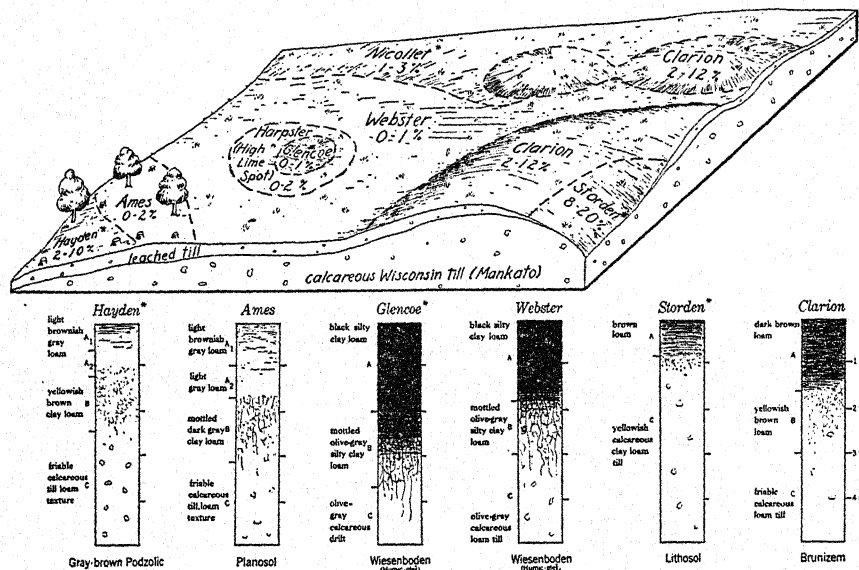


FIG. 1. PROFILES AND RELATIONSHIPS TO SLOPE AND VEGETATION OF MAJOR UPLAND SOILS IN THE CLARION-WEBSTER SOIL ASSOCIATION AREA OF IOWA

Adapted from "Principal Upland Soils of Iowa" (12). The Hayden and Ames series were developed under forest; the other soils were formed under prairie vegetation. Series names (above the profiles) marked with an asterisk are tentative, as is the name "Brunizem" for a great soil group. The latter has been proposed as a substitute for Brunigra soils (14).

MODERN CONCEPT OF THE SOIL TYPE

Soil types are still considered geographic bodies, but the concept is very different from that of 1899. In the modern concept, each area of a soil type is a small segment of the land surface extending downward into the earth for a few feet. Thus, each is a solid, usually with an irregular but easily observed surface, an indistinct lower boundary, and an evident but not sharply defined perimeter. Areas of soil types are like parts of the block diagrams commonly used to illustrate geological structures. Geographic relationships among soils in one landscape in Iowa are shown in figure 1. Because soil types are geographic bodies, each includes a large number of individual profiles, all of which occupy minute areas that are little more than points on the land surface. Each soil type, however, can be described in terms of its modal profile and the deviations from that

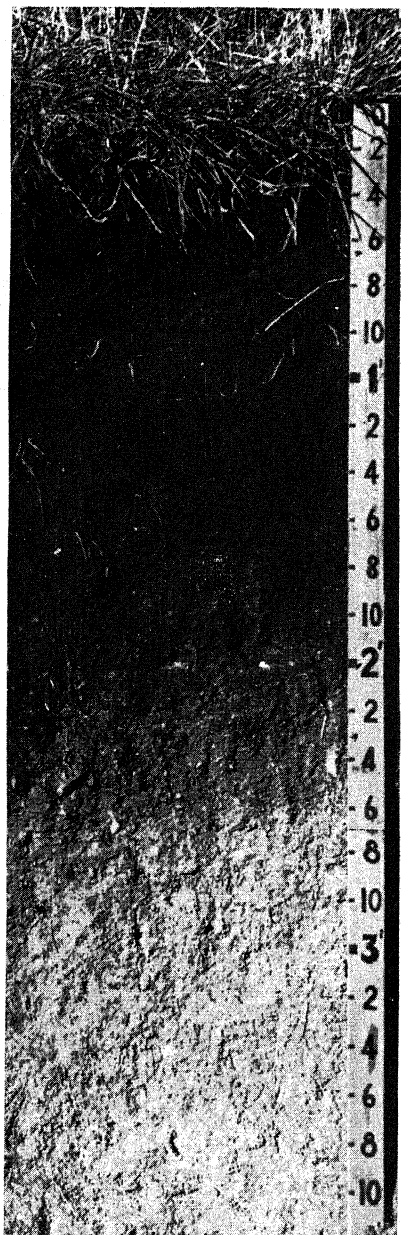


FIG. 2

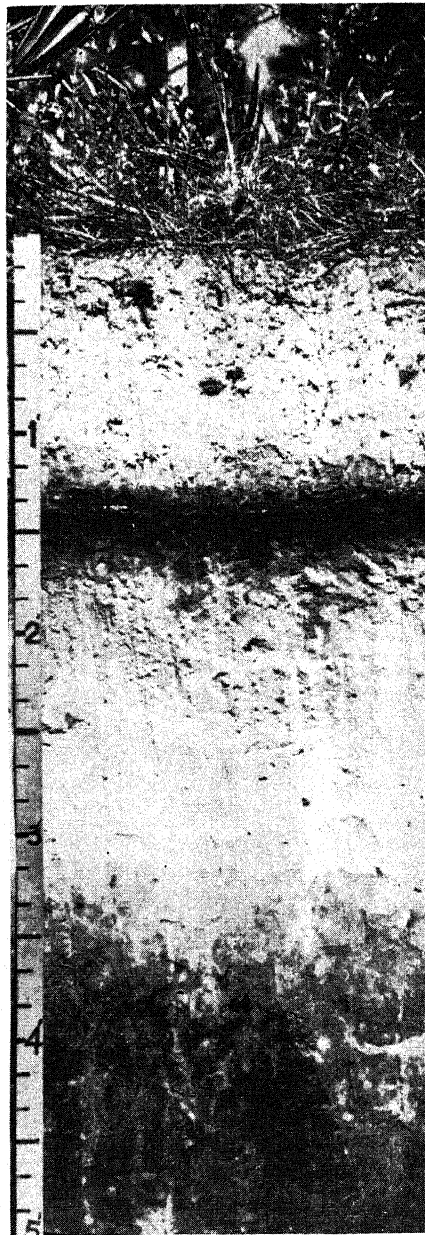


FIG. 3

FIG. 2. PROFILE OF WEBSTER SILTY CLAY LOAM, HUMIC-GLEI OR WEISENBODEN FORMED FROM CALCAREOUS GLACIAL TILL IN NORTHERN IOWA AND SOUTH-CENTRAL MINNESOTA

Note especially the thick, black A horizon and the lack of other distinct horizons.

FIG. 3. PROFILE OF LEON SAND, A GROUND-WATER PODZOL FORMED FROM ACID MARINE SANDS IN THE SOUTHERN STATES

Note the light colored A horizon, the thin black B horizon, and the almost white C horizon. The second dark layer at the bottom of the cut may or may not occur.

norm. It is a product of a unique combination of climate, living organisms, parent materials, topography, and time, often modified by man. Whenever a given combination of the factors of soil formation occurs, the soil type will be the same. This is of first importance in understanding soils and in predicting their behavior. It provides the opportunity for establishing a uniform system of classification and nomenclature that will allow the transfer of knowledge gained through research and experience in one place to similar soils in other places, whether those be in the same county or in different continents (6, 15).

Soil types (and phases) are defined in terms of soil properties, both internal and external, which are considered collectively. Major emphasis is given to the soil profile (a vertical section down through the soil to a depth of several feet), including its various horizons, because the profile is a reflection of the factors of soil formation, is important to the growth of plants, and has significance to engineering uses. A pair of strikingly different soil profiles are shown in figures 2 and 3.

The definitions of soil types and phases are based on differences in soil profile and on external features such as slope, degree of erosion, and stoniness. Characteristics considered in the definition of soil types and phases are directly observable or are inferred from observable features. The principal observable features considered are the number, thickness, and arrangement of horizons in a profile; the color, texture, structure, consistence, and reaction of each horizon; the contents of organic carbon, carbonates, and soluble salts in the soil; and the slope, stoniness, parent material, and underlying rock. The principal inferred properties considered are natural drainage, fertility levels, permeability, and degree of erosion. These features, and occasionally others, are all weighed together in the definition of individual soil types and phases, which are kept to the minimum consistent with sound classification in each area covered by a soil survey. It should be emphasized that the characteristics or properties of the soils and the interactions among those properties form the basis for the definition of soil types and phases, rather than the relationships of soils to factors of formation, to the growing of economic plants, or to their suitability for subgrades.

SIGNIFICANCE OF CHANGES IN CLASSIFICATION

Reflection of State of Knowledge

From comparisons of the scheme proposed in 1911 (5) with the concept of the soil type stated by Marbut in 1921 (8) and the present concept of the soil type (15), one useful lesson in soil classification is readily apparent. A scheme of soil classification reflects the state of knowledge in the soil science of its day. The categories in a scheme, the classes within categories, and the selection of criteria for differentiation depend upon the knowledge of soils at any given time. The proposed system in 1911 classified soils on a limited geological basis despite the criticisms offered by Coffey (3, 4). The theories of soil formation and the concept of the soil held generally at the time made a geological classification seem perfectly reasonable to most soil scientists. On the other hand, this approach in classification is clearly inadequate today.

The properties considered and the weights given to those properties in defining classes change with time. These changes come about for two reasons: first, more information about soils is gradually being accumulated; second, more is learned about the significance of the properties and their interactions to soil genesis and utilization. Fifty years ago a common parent material was an adequate basis for relating a number of soils as one soil type (18). Forty-five years ago the dark color of the surface layer was a sufficient basis for grouping soil types into series within a physiographic region (2). Neither of these bases seems adequate for defining soil types and series in 1950. These examples are but a few of these changes that have come with the growth of knowledge in the first half century of soil surveys.

Combinations of Characteristics

A very important lesson in the development of soil classification in the United States is that soil characteristics exist in combinations. Moreover, the significance of any one characteristic depends upon those with which it is associated. This lesson is not easy to learn. Nevertheless, it is there for all who study the evolution of the present scheme of classification. Among earlier proposals (4), there are schemes for classifying soils according to geological age of the rock formations, schemes keyed to the glacial age of sediments, and schemes tied to mode of transportation of soil materials. All of these schemes are based primarily upon one characteristic of the soil material. The inadequacies of these proposals are obvious as a result of the growth of knowledge about soils. It is generally recognized now that the soil profile with its horizons and their interrelationships must be considered in classification. This understanding has come gradually as more and more was learned about the soil.

The combinations of characteristics must be evaluated in constructing a classification. This is far harder than the job of considering one or perhaps two properties at a time. Yet it is of the first importance to see the significance of each soil characteristic in relation to those with which it is combined. To take but a single example, a high content of phosphorus is generally considered desirable, but it may have little meaning in some soils. The high levels of phosphorus in the Maury and similar soils in the Kentucky bluegrass region contribute greatly to the growing of race horses and fine cattle in that area. On the other hand, soils of Angaur Island in the west-central Pacific Ocean are not suitable for hand cultivation although they contain as much phosphorus as many phosphate ores. The high phosphorus content has little meaning because the shallow, stony character of the soil makes hand tillage impossible.

Limitations of Technical Groupings

Another lesson implicit in the history of the American soil survey is the need for basing classification on soil properties in combinations rather than on judgments as to possible usefulness of soils. Groupings of soils for specific practical objectives can be very useful, but they should not be expected to serve as comprehensive scientific schemes. The uses and limitations of such simplified schemes, often referred to as technical groupings, have been considered else-

where (11, 13). Experience with short-cut classifications has been generally unsatisfactory except for specific purposes. This is to be expected from the meanings of combinations of soil characteristics to use and management of the soils.

How soils are used depends not only upon their nature but also upon the state of the agricultural arts. As the agricultural arts change, soil characteristics take on different meanings. This is immediately and forcibly brought home to a soil scientist when he travels from one area with a mechanized agriculture to another area with similar soils in which cultivation is all by hand. Nevertheless, the suitability of soils for production of a single crop has been used as basis for defining units mapped in field surveys. As the crop production pattern changes with improved technology, the old interpretative classification becomes obsolete and cannot be reinterpreted in terms of new needs. Careful study of the development of classification and mapping procedures in the American soil survey will show the paramount importance of basing the definitions of the units on the properties and the combinations of properties of the soils themselves.

Selection and Weighting of Criteria

Finally, it is clear from the development of soil classification that a central and continuing problem is one of selecting and weighting properties in differentiating classes and categories. The choosing of properties and the weighting of them in combinations is the principal question that will plague soil scientists as long as classifications are attempted. What properties shall be used to distinguish soil types from one another? How much weight shall be given to the different properties in this combination? This choosing and weighting of soil properties in constructing a classification is the hardest part of the job. It is done within a frame of reference that consists of the theories of genesis and the knowledge of morphology and behavior in the minds of the scientists making the classification. In other words, the construction of a classification is circumscribed by the knowledge of soils and their genesis held by the scientists responsible for the scheme. This central problem in soil classification will last as long as the efforts to classify soils. It is important at all times to recognize this and to realize that the answers obtained will sooner or later be superseded. Thus, the pattern is one of improving an approximation of the ideal. As the body of knowledge in soil science changes, so must soil classification change. This is accomplished through shifts in the scheme and through shifts in the selection and weighting of criteria for differentiating classes and categories. This lesson is one of the most important that can be drawn from this first half century of soil surveys in America.

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BOOKS

Agricultural Geography of the World. By J. PAPADAKIS. Published by Author, Nahuel, Huape 4984, Buenos Aires, 1952. Pp. 118, plates 3, maps 4. Paper-bound.

The author has undertaken a very large task in organizing crop plant information in terms of climate, growth rate and rhythm, vegetation, soils, and agricultural regions. The first chapter is devoted to temperature, light, water, and edaphic conditions. The second chapter gives an ecological classification of crops. The third chapter considers crop climate in terms of winter hardiness, summer duration and heat, and humidity and its seasonal distribution. In chapter 4 a formula is set down by which a world map of growth rate and rhythm was developed. Chapter 5 deals with soil formation in relation to plant geography. The agricultural regions of the world are shown in chapter 7. A bibliography of some 150 references and excellent sets of plates and maps are appended. A number of errors in spelling and language are found, but these are minor matters. The general concepts are good, and the approach to the subject is that of a highly capable scholar.

Bacteria. By STANLEY THOMAS AND THOMAS H. GRAINGER. The Blakiston Company, New York, 1952. Pp. 623. Price \$5.50.

The authors of this book have done an exceptionally good job in developing an interesting and instructive text that should prove highly useful in colleges and universities. The 35 chapters cover a wide range of topics, including not only taxonomy, morphology, and cytology of bacteria and their respiration, nutrition, metabolism, and ecology, but enzymes, rickettsiales, virales, bacteriophages, bacteria in soil, water, sea, sewage, air, foods, and industry, and pathogens, immunity, chemotherapy, antibiotics, and bacterial warfare. A number of excellent illustrations, designed to show bacteriology in practice, are included. Long lists of references are given at the ends of the chapters, and the appendix contains a classification of bacteria. The authors are to be congratulated on having succeeded in presenting the subject in such an attractive manner.

DDT and Newer Persistent Insecticides. Second Edition. By T. F. WEST AND G. A. CAMPBELL. Chemical Publishing Co., Inc., New York, 1952. Pp. 632, plates 13. Price \$8.50.

DDT (dichloro-diphenyl-trichloroethane) was first made in 1874, but it was not used as an insecticide until 1939, when Paul Müller of the Basle laboratories of J. R. Geigy S. A. discovered its great value. The authors deal with the original researches on DDT, its manufacture, principles of formulation, use in paints, textiles, and paper, and against lice, mosquitoes, and a great variety of other insects affecting man, animals, and plants. Special attention is paid to the effect of DDT on beneficial insects, notably the honeybee. The authors indicate that it may be possible completely to eliminate the tsetse fly by the use of DDT.

Some 65 pages are devoted to benzene hexachloride, chlordane, toxaphene, and four new insecticides. References are appended to each chapter, and a supplemental long list is given in the appendix, complete to 1948. The plates merit special mention. The book is an excellent reference work for all those who have to do with direct or indirect effects of these insecticides.

A Dutch Fork Farm Boy. By J. M. ELEAZER. University of South Carolina Press, Columbia, 1952. Pp. 154, plates 5. Price \$3.50.

For those who were born on a farm out in the open country 50 or more years ago, this book will bring back many memories of the days when boys went barefooted, walked a mile or so to school, took plenty of time off for fishing, watched the first automobile go by, and enjoyed a great variety of Nature's fruits fresh from vine, bush, or tree. Those were the days of husking bees, community butchering, soap making, possum hunting, rabbit trapping, and occasional trips to the big city. They were also the days of the old oaken bucket, the village blacksmith, mud roads, and hoeing long rows of corn and cotton. All of these and the daily doings of one boy are amusingly reported in this delightfully told story.

Genetics in the 20th Century. Edited by L. C. DUNN. The Macmillan Company, New York, 1951. Pp. 634. Price \$5.

The invitation papers presented on the program of the Golden Jubilee of Genetics at The Ohio State University, Columbus, September 11-14, 1950, make up this volume. The speakers were Goldschmidt, Iltis, Zirkle, Castle, Muller, Sturtevant, Mather, Mirsky, Caspersson, Schultz, Irwin, Beadle, Ephrussi, Lederberg, Sonneborn, Darlington, White, Snyder, Penrose, Gowen, Little, Müntzing, Lush, Walker, Mangelsdorf, Dobzhansky, and Huxley. Goldschmidt, speaking on "The Impact of Genetics on Science," drew attention to the rapid developments in this science during the last 50 years and their impact on every branch of biology. Huxley, speaking on "Genetics, Evolution, and Human Destiny," pointed out that the most significant characteristic of the process of natural selection was that it continued to reveal new possibilities inherent in living matter. He concluded that geneticists may well be proud of the part they have played in developing new concepts of human destiny, that ignorance is one of the chief obstacles to human advancement, that we need more well-integrated human personalities, and that we can look forward with optimism to a reconciliation of the world's warring political and social ideologies. This is an important book that merits wide reading. Long lists of excellent references are appended to many of the papers.

Improving the World's Grasslands. By A. T. SEMPLE. Leonard Hill Limited, London, 1952. Pp. 147, figs. 107. Price, paper-bound, 10/6.

The author of this book is agricultural officer of the animal production branch of the FAO. He was assisted by about 50 contributors. The 10 chapters deal with importance of grassland, place of grass in agriculture, rangeland improvement, livestock management, seeding and fertilizing, mechanical treatment and

burning, national grassland programs, fodder from trees and shrubs, supplemental feeding, and need for research. The illustrations constitute one of the most interesting parts of the book. A list of references is appended to each chapter.

Isotopes. United States Atomic Energy Commission, Oak Ridge, Tennessee, 1951. Pp. 451. Paper-bound.

This is a 5-year summary of distribution of isotopes, with a bibliography of 1,402 papers. Among the many matters discussed are isotope distribution, production, processing, stockpiling, procurement, allocation, export, import, training in techniques, and possible future uses. The appendix contains tables of isotope distribution and lists of published papers in relation to the use to which the isotopes are being put.

Laboratory Manual for General Bacteriology. Fourth Edition. By GEORGE L. PELTIER, CARL E. GEORGI, AND LAWRENCE F. LINDGREN. John Wiley and Sons, Inc., New York, 1952. Pp. 293. Price, board cover, spring back, \$3.05.

The 60 laboratory exercises in this text are designed to meet the needs of students of diverse interests, with special reference to bacterial functions. Each exercise outlines the purpose, indicates materials required, shows procedure, calls for record of results, asks some questions, and gives some references for supplemental reading. The exercises cover structure, chemical composition, metabolism, factors influencing growth, and sanitary, dairy, food, soil, and disease-producing microorganisms. The appendixes contain illustrations of descriptive terms, formulas for staining solutions, reagents, and media, bibliography, and index of microorganisms. This is an excellent laboratory manual.

Manures and Fertilizers. By British Ministry of Agriculture and Fisheries. Chemical Publishing Co., Inc., New York, 1952. Pp. 95. Price \$2.50.

The first issue of this publication was in the form of a bulletin designed to aid in better use of manures, fertilizers, and soil amendments on British farms. Now in book form, about half of it is devoted to the preservation and use of animal manures, various other kinds of organic wastes, and green manures. Instructions are given for storing urine and for producing artificial manures from straw. A discussion of seaweeds is of special interest. White mustard or green globe turnips, with or without rape, are suggested for heavier land as summer green-manures following fallow. Recommendations are made for the use of fertilizers on each of the more important crops. Special instructions for storing fertilizers are given. The appendix contains an abstract of the British fertilizers and feeding stuffs act. The book is of particular interest for comparison with manuring and fertilizing practices in the United States.

The Origin of Life and the Evolution of Living Things. By OLAN R. HYNDMAN. Philosophical Library, New York, 1952. Pp. 648. Price \$8.75.

The purpose of the author of this highly illuminating philosophical discussion on evolution is to develop the theory of multiple and continuous changes in

germ plasm as a result of the continuous operation of environmental influences. Cause and effect relationships are said to apply to development of living things in much the same manner as they do to happenings in chemistry and physics in the inanimate world. The author cannot accept the concept of fortuitous mutation which tends to dominate the point of view of most biologists. The four sections of this well-reasoned presentation deal with hypotheses concerning the origin of living matter, the various mechanisms involved in reproduction, past and present theories of evolution, and the proposed theory with which the book is primarily concerned. The final chapter presents a very interesting statement on senescence and death of the individual. A bibliography of 39 references is appended. This is an important book.

Pathology in Forest Practice. Second Edition. By DOW VAWTER BAXTER. John Wiley and Sons, Inc., New York, 1952. Pp. 601, figs. 224. Price \$7.50.

The 10 chapters in this book deal with the nature of disease in forests, the damage resulting therefrom, the relation of practice to disease incidence in nurseries and mature forests, shade and park tree diseases, handling of forest products, and wood discolorations. The new edition gives recent information on pole blight in the northern Rocky Mountains, dieback in New England birch, little-leaf disease in the Piedmont, virus diseases, and the use of DDT and 2,4-D. The material is well presented. The illustrations are excellent and well chosen. A long list of references is appended to each chapter. Considerable attention is given to tree adaptation in relation to soil and climatic conditions. An exceptionally good index is appended, in which one can find a reference to almost any pathological or related matter on trees that may be of interest to him. The book should prove a very welcome addition to modern literature in this field.

Poisons, Their Chemical Identification and Emergency Treatments. By VINCENT J. BROOKES AND HUBERT N. ALYEA. D. Van Nostrand Company, Inc., New York, 1946.

Extensive use of poisonous materials for the control of farm pests requires that more soil-plant scientists be advised concerning the possible effects of these materials on humans and the best means of treatment in case of emergency. Although the authors of this book were not especially concerned with agricultural poisons, their general treatment of the subject provides much useful information. It is interesting to note that of the deaths reported from poisoning, the largest percentage of the suicides are from illuminating gas and the greatest proportion of accidental deaths from alcoholism. But there are a number of cases of accidental poisoning from cyanides, arsenicals, sodium fluoride, carbon tetrachloride, and a variety of related compounds. The book has great value for ready reference.

Principles of Geochemistry. By BRIAN MASON. John Wiley and Sons, Inc., New York, 1952. Pp. 276, figs. 42. Price \$5.

This highly interesting and informative book has for its purpose the study of the relative and absolute quantities of the elements and atomic species in the earth and of their distribution and migration. Following an explanatory introduction, the several chapters deal with the earth in relation to the universe, structure and composition of the earth, thermodynamics and crystal chemistry, magmatism and igneous rocks, sedimentation and sedimentary rocks, the hydrosphere, atmosphere, and biosphere, metamorphism and metamorphic rocks, and the geochemical cycle. To uncover the laws that control the distribution of the individual elements requires a study of large masses of analytical data on terrestrial material, meteorites, and other cosmic bodies and consideration of the earth's interior. The data and conclusions in the book are of great interest and value to soil scientists. A very useful list of selected references is appended to each chapter.

Reclamation in the United States. By ALFRED R. GOLZE. McGraw-Hill Book Company, New York, 1952. Pp. 437. Price \$8.

The author of this book is director of programs and finance for the Bureau of Reclamation. The discussion largely concerns irrigation of arid lands and the many related problems. The area of such land was set at approximately 25 million acres in 1949. The several chapters have to do with economics, law, agencies, projects, river-basin development, cost allocations, repayment by farmers, power companies, and others, cost estimating, accounting, settlement, operation, and maintenance. The appendix shows irrigation statistics by states. This is the most comprehensive and readable review of the subject that has come to our attention.

Rural Brazil at the Crossroads. By H. MEIJER. H. Veenman and Zonen, Wageningen, The Netherlands. Pp. 208, maps 3, figs. 13. Price \$2.50.

This book outlines the early history of rural Brazil and, with this as a background, indicates what changes must take place and why, how these changes could be stimulated, some of the favorable and unfavorable factors, developments that would be most advantageous to the country, and probable consequences of such developments. The author points out that Brazil has a larger area than the United States, including Alaska. Its climate is predominantly tropical. Its population, totaling 53 million, is 30 per cent Latin white, 30 per cent mulattoes, and 15 per cent Indians. The people are said to lack "team spirit," "staying power," and "moral courage." There is need for widespread education, notably among the black races. "Most of the land now under cultivation needs continual gifts of manure, complemented by considerable amounts of fertilizers, to give regular crops and preserve the topsoil. Only a small part of the potential agricultural lands is used as such." About 90 per cent of the cultivated area, totaling 17 million acres, is devoted to cotton, rice, coffee, sugar cane, beans, manioc, and maize. Brazil is the first cattle-raising country of South America and the third in the world. Protection of the soil against wind and water erosion is of greatest importance. It is suggested that concen-

tration of intensification should be made near urban centers. Credit facilities should be improved. Better living conditions are needed.

Soil Development. By EDWARD H. FAULKNER. University of Oklahoma Press, Norman, 1952. Pp. 232. Price \$3.

Income from the sale of 340,000 copies of "Plowman's Folly" made it possible for the author to devote more time to travel, reading, and experimentation in preparation for the publication of three additional books, of which this is the latest. In this book he develops the thesis that it is not necessary to use lime, fertilizer, compost, or any other soil amendment, save the refuse of crops and cover crops. These crop wastes are worked into the surface soil rather than being plowed under. During the first 4 years of this program on his experimental farm, the crops were not impressive, and considerable trouble was experienced with insects and diseases. In the fifth year, however, tomatoes yielded at the rate of 21 tons an acre, and head lettuce gave excellent results. Mexican bean beetles passed his plantings by in favor of those of his neighbors. The author does not advise against the use of fertilizers. Rather, he suggests that farmers would do well to use them while bridging the gap between plow-plus-mineral economy and that of the toolbar cultivator-plus-crop refuse. When this change has finally been effected, crop yields, he believes, will be higher and food will be better and cheaper.

Soil Physical Conditions and Plant Growth. Edited by BYRON T. SHAW. American Academic Press, Inc., New York, 1952. Pp. 491, figs. 96. Price \$8.80.

This is volume 2 of a series of monographs prepared under the auspices of the American Society of Agronomy. The material was compiled by the Joint Committee on Tilt of that Society and the American Society of Agricultural Engineers. The contributors are L. T. Alexander, R. M. Hagan, J. F. Lutz, T. M. McCalla, H. E. Middleton, L. A. Richards, S. J. Richards, M. B. Russell, Byron T. Shaw, and C. H. Wadleigh. The papers deal with soil as a physical system, mechanical impedance and plant growth, and soil water, soil aeration, and soil temperature and plant growth. The material is well arranged and presented and constitutes a highly important contribution to the literature in this field. A bibliography of about 400 very useful references is appended.

Soils and Soil Fertility. By LOUIS M. THOMPSON. McGraw-Hill Book Company, Inc., New York, 1952. Pp. 339, figs. 136. Price \$5.

The author designed this book for use in teaching the subject on a one-semester basis at Iowa State College. The point of view of every author in the agricultural field is determined largely by the environment in which he is experienced. That applies to this book. It covers the nature and properties of soils, physically, chemically, biologically, and mineralogically, and the practices and amendments that are applied to them to maintain and increase their productivity. The illustrations are well chosen and add greatly to the value of the book, as do the 132 tables of very informative experimental data. The author is to be congratulated on having developed such an attractive and excellent textbook.

Spectrochemical Procedures. By CHARLES E. HARVEY. Applied Research Laboratories, Glendale, California, 1950. Pp. 402. Price \$7.50.

The author of this book has rendered an exceptional service in carefully describing and illustrating the techniques employed in spectrographic procedures and in offering many suggestions that are of great aid in making and recording the analyses. He defines the terms employed, describes the instruments, tells how to calibrate, gives the general features of the spectra of various elements, advises on qualitative, semiquantitative, and quantitative procedures, gives directions on establishing standards, shows how calculations are made, indicates the variables to be dealt with, and gives instructions on setting up a laboratory. It is quite apparent that the author has had abundant experience in this method of analysis. The book gives the clearest presentation of the subject of any so far reviewed.

Textbook of Electrochemistry. Volume 1. By G. KORTÜM AND J. O'M. BOCKRIS.

Elsevier Publishing Company, New York, 1951. Pp. 351, figs. 48. Price \$7.

This translation and revision of the second (1949) German edition of Kortüm's "Lehrbuch der Electrochemie" is designed for university students. The first two chapters outline the general principles of electrochemistry and the derivations of the fundamental equations. These are followed by chapters on solvation of ions, weak and strong electrolytes, theory of interionic attraction, application of conductance measurements, electromotive force, applications of potentiometric measurements, and equilibria in solutions of weak electrolytes. A second volume, to appear later, will deal with electrical phenomena at interfaces, irreversible electrode processes, gases, and experimental methods, with appended tables of physicochemical quantities. The chapter on potentiometric applications in volume 1 is of special interest to soil-plant scientists, particularly the material on significance of pH, quinhydrone, glass and oxide electrodes, and oxidation-reduction reactions. This is a highly valuable reference book.

Water. By CYRIL S. FOX. The Philosophical Library, Inc., New York, 1952. Pp. 148, figs. 4, plates 25. Price \$8.75.

The author deals with the properties, circulation, and utilization of water in this book, first of a series on geology of water supplies, water treatment, sewage disposal, water supplies of towns, construction of water works, drilling rigs, and wells. A large quantity of very useful data has been assembled. Included among these data are analyses of fresh, lake, runoff, and sea waters, comparison of properties of ordinary and heavy waters, output of important rivers, precipitation at various locations, and properties and discharges of filter beds. The plates show excellent views of important natural water supplies and construction for their control, such as Niagara Falls, Victoria Falls, Grand Coulee Dam, and various hot springs. Among the figures are one of a coastal plain water supply, another of a silted-up valley, and a third of the Tennessee Valley profile. The material is presented in a semipopular form. The book should be of much interest to a considerable variety of scientists.

THE EDITORS

SOIL SCIENCE

VOLUME 74

October 1952

NUMBER 4

CLAY MINERALS OF FOUR SOUTHERN NEW YORK SOILS

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Received for publication July 30, 1951

Experience has shown that estimates of the clay mineral composition of soils are most reliable when they are based on measurements of several properties. In this study, estimates of the mineralogical composition of four soils from southern New York were made by comparing several properties of the soil clay with those of reference clay minerals. The properties used in these comparisons were differential thermal analysis, ethylene glycol retention, total potassium content, cation-exchange capacity, and x-ray analysis.

MATERIALS AND METHODS

The soils studied were the Bath, Mardin, Volusia, and Chippewa, all members of an important drainage catena from southern New York. Each of the soils has been developed under forest vegetation on late Wisconsin till derived from acid gray sandstones and shales. The climate in Tompkins and Tioga Counties where these samples were collected is cool and humid. The profile characteristics at the depths at which the samples were taken are described briefly in table 1.

Samples of montmorillonite, kaolinite, illite, chlorite, and vermiculite were obtained from commercial sources.¹ These minerals were examined with respect to each of the several properties listed and were used as standards in the estimation of the mineralogical composition of the soil clays. The montmorillonite, kaolinite, and illite reference minerals used are from type localities listed by Kerr *et al.* (5).

Material $<5.0 \mu$ was separated from each sample of montmorillonite, kaolinite, and illite by gravity sedimentation after dispersion with Na_2CO_3 and a mechanical stirrer. The fractionation was repeated five times and gave a suspension which contained more than 95 per cent of the material $<2.0 \mu$ that was present in the original samples. This suspension was divided into subsamples having sizes 2-1, 1-0.5, 0.5-0.2, and $<0.2 \mu$ as calculated on the basis of effective settling diameters. The first of these size classes was separated from the bulk suspension by repeated gravity sedimentations. The others were obtained by use of a Sharples supercentrifuge. In each case the separations were repeated until a mechanical

¹ Montmorillonite: Wyoming volclay from American Colloid Co., Chicago. Kaolinite: Peerless #2, Bath, S. C., from R. T. Vanderbilt Co., New York City. Illite: Grundite, Goose Creek, Illinois, from Illinois Clay Products Co., Joliet. Chlorite: Chester, Vt., from Wards Natural Science Est., Rochester, New York. Vermiculite: from Wards Natural Science Est., Rochester, New York.

analysis showed that less than 10 per cent of the material within the subsample was beyond the specified limits. The chlorite and vermiculite were merely ground

TABLE 1
Profile descriptions of four southern New York soils

SAMPLE NUMBER	PROFILE	HORIZON	SAMPLING DEPTH	DESCRIPTION
B ₁	Bath silt loam (well-drained, moderately developed gray-brown podzolic)	Ap	<i>inches</i> 2-8	Brown. Loose crumb structure
B ₂		B ₂	14-18	Yellowish brown with weak fine crumb structure. Friable
B ₃		B ₃	20-24	Light yellowish brown. Firm
B ₄		C	30+	Grayish brown, firm, medium thick, platy glacial till
M ₁	Mardin silt loam (moderately well drained, weakly developed gray-brown podzolic)	Ap	2-4	Grayish brown. Loose and friable
M ₂		B ₂	8-10	Yellowish brown. Very friable. Well aerated and rich in iron oxides
M ₃		B _{g1} *	11-14	Light yellowish brown mottled with yellowish brown and light brownish gray. Weak crumb structure
M ₄		B _{g2} *	20-24	Gray mottled with yellowish brown. Very firm. Dense
M ₅		C	40+	Grayish brown, firm, weakly platy glacial till
V ₁		Ap	2-4	Gray. Fairly loose. Grayish brown with very weak medium, crumb structure
V ₂	Volusia silt loam, (poorly drained, low-humic glei)	BG ₁	7-10	Blocky structure. The insides of blocks are mottled gray and yellowish brown
V ₃		BG ₂	14-18	Light brownish gray with weakly moderate, coarse blocky structure
V ₄		C	36+	Grayish brown, hard, coarse platy glacial till
C ₁		Ap	2-6	Very dark gray. Organic matter in various stages of decomposition mixed with silt
C ₂	Chippewa silty clay loam (very poorly drained, humic glei)	G	10-14	Dark gray. Essentially like A, but less organic matter. Material somewhat compact with slight rust mottling
C ₃		CG	24+	Grayish glacial till, virtually unweathered

* The _g indicates slightly gleied.

to pass a 300-mesh screen. After fractionation, all samples were treated with H₂O₂ to remove organic matter and were saturated with calcium from calcium

acetate. After removal of excess salts with 95 per cent ethyl alcohol, the samples were air-dried, ground to pass a 100-mesh sieve, and stored in a closed chamber at a relative humidity of 31 per cent.

The differential thermal analyses were made with an apparatus patterned after that described by Kerr *et al.* (5).² Medium sensitivity and a heating rate of 12.5° per minute were used. Temperature checks were provided at 575, 810, and 890°C. by a reference mixture composed of equal weights of quartz and BaCO₃. Where necessary, the thermal curves of the unknown samples have been adjusted to fit these reference points. After completion of each differential thermal run, the sample was allowed to cool to approximately room temperature and then reheated to 700°C. This rerun was used as a base line for the initial curve and also as a means of detecting the presence of quartz, which undergoes a reversible endothermic reaction at 575°C.

The hydratable surface of the soil clays and reference clay minerals was determined by the ethylene glycol retention method of Dyal and Hendricks (1). Best results were obtained when this measurement was conducted in a lighted room at a constant temperature of 25°C.

The total potash content of the samples and reference materials was determined by the J. L. Smith fusion procedure (6, pp. 748-752). The sintered mass was dissolved to give a known volume of solution, and potassium was determined by means of a Perkin-Elmer flame photometer.

Cation-exchange capacity was determined by an ammonium acetate leaching procedure (7, pp. 9-11). The samples were first saturated with NH₄⁺ by use of 1.0 *N* ammonium acetate at pH 7.0, and the excess salt was removed by leaching with 95 per cent ethyl alcohol. The NH₄⁺ after having been removed with an acidified 10 per cent NaCl solution was determined by nesslerization.

X-ray patterns were obtained on representative samples with an x-ray spectrophotometer. The samples were pretreated to remove iron oxides and were saturated with glycerol.

RESULTS

The particle size distribution of the several profile samples and of the three principal clay minerals studied is summarized in table 2. This shows that the amount of material greater than 2.0 mm. ranges from about 15 to 50 per cent in each of the profiles except the Chippewa. This percentage tends to increase with depth in the profile. In the Bath, Mardin, and Volusia profiles the percentage silt shows a rather consistent decrease with depth, whereas in the Chippewa it is largely independent of the depth of sampling. The clay content tends to decrease with depth in the Bath, Volusia, and Chippewa profiles but is not consistent in the Mardin.

The total clay is rather uniformly distributed among the four subfractions, although there is some tendency for the proportion in the finest fraction to be greater in those samples having the highest total clay content. The kaolinite and

² The authors are indebted to T. W. Lamb for use of the excellent differential thermal equipment in his laboratory at the Massachusetts Institute of Technology.

illite also are fairly uniformly distributed throughout the four size classes, whereas the montmorillonite distribution is highly skewed toward the finer end of the clay fraction.

The differential thermal curves for the reference clay mineral samples are shown in figures 1 and 2. These curves, which are typical for the reference minerals used, show characteristics that are essentially independent of particle size. The irregularities in curve 1D suggest the presence of fine-grained impurities in this sample. In the same curve the shift of the 600°C. endothermic reaction to a slightly lower temperature suggests a reduction in the degree of crystallinity of

TABLE 2
Mechanical analysis of soils and reference clays

SAMPLE	DEPTH	STONES, >2.0 MM.	SAND, 2000-50 μ	SILT,* 50-2.0 μ	CLAY				
					Total	2-1 μ	1-0.5 μ	0.5-0.2 μ	<0.2 μ
	<i>inches</i>	%	%	%	%	%	%	%	%
Bath 1.....	2-8	18.4	8.8	54.0	18.8	3.9	4.9	4.5	5.5
2.....	14-18	30.7	8.6	47.5	13.2	4.7	5.0	2.0	1.5
3.....	20-24	30.1	24.9	39.0	6.0	2.0	2.1	0.3	1.6
4.....	30-36	40.2	13.5	35.4	10.9	3.4	3.2	1.5	2.8
Mardin 1.....	2-4	34.6	15.3	35.6	14.5	3.4	2.2	4.0	4.9
2.....	8-10	29.3	16.8	38.7	15.2	3.8	2.1	4.4	4.9
3.....	11-14	26.9	24.8	37.0	11.3	2.8	1.1	3.8	3.6
4.....	20-24	48.8	14.0	23.3	13.9	2.6	1.6	4.7	5.0
5.....	40-46	39.9	19.0	25.3	15.8	2.9	1.8	5.7	5.4
Volusia 1.....	2-4	14.8	7.9	56.3	21.0	4.7	5.5	4.1	6.7
2.....	7-10	11.5	9.4	60.9	18.2	4.2	5.8	4.0	4.2
3.....	14-18	33.3	10.0	42.5	14.2	3.4	3.3	2.4	5.1
4.....	36-40	52.5	8.7	23.8	15.0	3.7	4.1	2.5	4.7
Chippewa 1.....	2-6	<0.5	23.2	56.8	20.0	3.6	1.7	6.6	8.1
2.....	10-14	5.0	23.6	55.2	16.2	4.0	4.7	2.0	5.5
3.....	24-30	9.5	18.0	55.0	17.5	4.6	3.8	3.7	5.4
Kaolinite.....	—	—	—	—	100	19.2	29.2	27.2	24.4
Illite.....	—	—	—	—	100	26.5	25.4	13.5	34.6
Montmorillonite.....	—	—	—	—	100	2.7	16.5	22.8	58.0

* Silt by difference.

the finely divided kaolinite. The shift of the endothermic reaction of montmorillonite from 750 to 700°C. in curve 1G is generally interpreted as the result of an increased substitution of iron in the crystal lattice. The curves for illite shown in figure 2 are in general agreement with those that have appeared in the literature. The small exothermic reactions in the neighborhood of 350°C. shown in curves 2C and 2D suggest that hydrated iron or aluminum oxides may be present in the finer fractions of illite.

Curve 2E shows that in mixtures of kaolinite and illite, the 600°C. kaolinite reaction completely masks the smaller illite reaction that occurs at about the same temperature. The 875°C. illite peak, however, is unaffected by the presence

of kaolinite and is useful as an indication of the amount of illite present. Curve 2F shows that in mixtures of illite and montmorillonite there is little or no interaction between the 600°C. reaction of illite and the 740°C. reaction of montmorillonite. Curve 2G shows that in mixtures containing all three of the principal clay minerals no additional interactions occur other than that between kaolinite and illite previously discussed.

The differential thermal curves for the Bath profile, taken as representative of the soil clays, are shown in figure 3. The general similarity of all the curves is

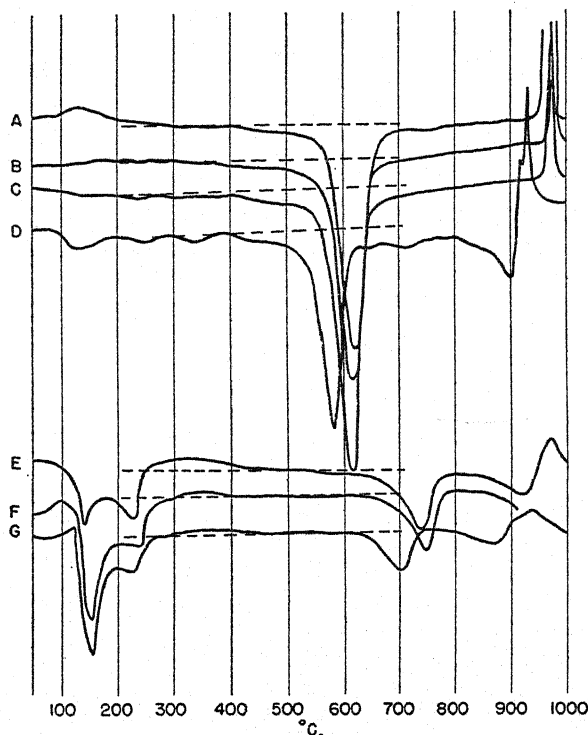


FIG. 1. DIFFERENTIAL THERMAL CURVES FOR THE REFERENCE CLAYS KAOLINITE AND MONTMORILLONITE

A, kaolinite 2-1 μ ; B, kaolinite 1.0-0.5 μ ; C, kaolinite 0.5-0.2 μ ; D, kaolinite <0.2 μ ; E, montmorillonite 1.0-0.5 μ ; F, montmorillonite 0.5-0.2 μ ; G, montmorillonite <0.2 μ .

at once apparent, indicating that there are no marked differences in mineralogical composition among the four soils or between depth or size fractions within the soils. The absence of the sharp endothermic peaks at 600°C. and about 740°C. indicate that kaolinite and montmorillonite are not major constituents of these soil clays. It has been shown that 10 to 15 per cent of either of these minerals can readily be detected from differential thermal curves (3). It is concluded, therefore, that kaolinite and montmorillonite, if present, are in amounts less than 10 per cent.

The broad endothermic reactions having a minimum at 550° to 600°C. are attributed to illite, although in some instances chlorite might be present. The exothermic reaction in the 700–850°C. region is ascribed to chlorite because, although siderite also gives an exothermic peak in this region, CO₂ determinations indicated that carbonates were not present.

The endothermic and exothermic peaks in the range from 300–500°C. which are most prominent in the finer fractions of the soil clays are attributed to hydrated oxides of iron and aluminum. The dotted rerun curves for the course clay

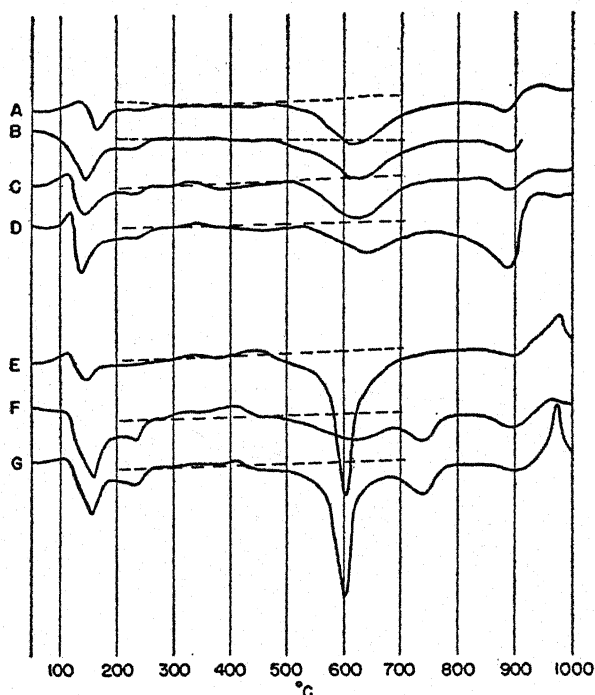


FIG. 2. DIFFERENTIAL THERMAL CURVES FOR THE REFERENCE CLAY ILLITE AND MIXTURES OF REFERENCE CLAYS

A, illite 2–1 μ ; B, illite 1.0–0.5 μ ; C, illite 0.5–0.2 μ ; D, illite <0.2 μ ; E, two-thirds illite, one-third kaolinite (0.5–0.2 μ); F, two-thirds illite, one-third montmorillonite (0.5–0.2 μ); G, one-third illite, one-third kaolinite, one-third montmorillonite (0.5–0.2 μ).

fractions show a dip at 575°C., indicating the presence of quartz. Several such samples were rerun at high sensitivity and from the resulting curves it was estimated that the amount of quartz present was approximately 10 per cent.

The ethylene glycol retention data for the fractionated soil clays and the reference clay minerals are summarized in table 3. Except for the normal increase in internal surface with decreasing particle size, there seem to be no consistent trends in the internal surface area calculated from the glycol retention data. In two of the <0.2 μ samples the ethylene glycol retention of the heated specimen exceeded that of the unheated sample. Since these two samples also had abnormal

differential thermal curves, it was concluded that they contained some contaminating substance. The internal surface areas of the vermiculite and chlorite samples that had been ground to pass a 300-mesh screen were 122 and 40 sq. m. per gram, respectively.

The total potash contents of the soil clays and of illite are summarized in table 4. These data indicate that many of the soil clays contain a higher percentage of

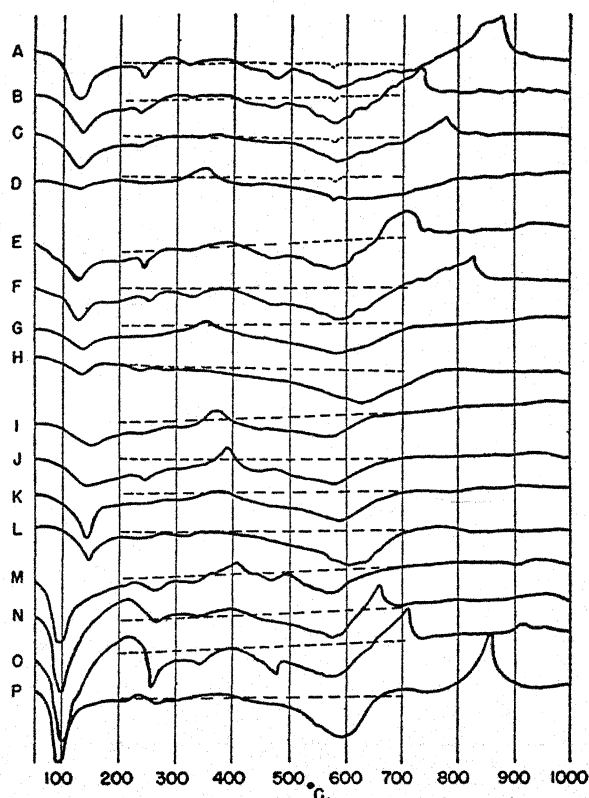


FIG. 3. DIFFERENTIAL THERMAL CURVES FOR THE BATH PROFILE

A, sample B₁ 2-1 μ ; B, sample B₂ 2-1 μ ; C, sample B₃ 2-1 μ ; D, sample B₄ 2-1 μ ; E, sample B₁ 1-0.5 μ ; F, sample B₂ 1-0.5 μ ; G, sample B₃ 1-0.5 μ ; H, sample B₄ 1-0.5 μ ; I, sample B₁ 0.5-0.2 μ ; J, sample B₂ 0.5-0.2 μ ; K, sample B₃ 0.5-0.2 μ ; L, sample B₄ 0.5-0.2 μ ; M, sample B₁ <0.2 μ ; N, sample B₂ <0.2 μ ; O, sample B₃ <0.2 μ ; P, sample B₄ <0.2 μ .

potash than did the sample of illite used as a reference material. Grim *et al.* (2) have reported that the potash content of illite ranges from 4.7 to 6.9 per cent and that of "illite-like" minerals ranges up to 9.5 per cent. The soil clays, therefore, are still well within the range of illite. There was a tendency for the potash content to increase with depth for all the profiles. In most of the samples the total potash content was lowest in the <0.2 μ fraction.

The cation-exchange capacity data, summarized in table 5, also show an in-

TABLE 3
Ethylene glycol retention and calculated internal surface areas for soil and reference clays
Per gram

SAMPLE	2-1 μ			1.0-0.5 μ			0.5-0.2 μ			<0.2 μ		
	Glycol retention		Internal surface	Glycol retention		Internal surface	Glycol retention		Internal surface	Glycol retention		Internal surface
	Unheated	Heated to 600°		Unheated	Heated to 600°		Unheated	Heated to 600°		Unheated	Heated to 600°	
	mgm.	mgm.	sq. m.	mgm.	mgm.	sq. m.	mgm.	mgm.	sq. m.	mgm.	mgm.	sq. m.
Bath 1	24.7	8.3	52.9	33.8	14.4	62.6	35.0	19.8	49.0	78.1	24.6	173
2	22.3	8.9	43.2	31.6	13.0	60.0	39.6	20.4	61.9	84.5	28.6	180
3	21.6	6.0	50.3	22.4	11.6	34.8	42.1	18.4	76.4	72.0	34.3	122
4	11.0	3.7	23.5	17.9	5.4	40.3	25.3	8.1	55.5	56.8	21.3	114
Mardin 1	25.2	9.4	51.0	24.5	8.3	52.2	35.4	13.0	72.3	56.6	43.5	42.2
2	22.0	5.7	52.6	29.4	11.3	58.4	34.5	14.9	63.2	62.4	27.6	112
3	13.4	3.1	33.2	19.2	5.7	43.5	26.0	7.8	58.7	48.0	23.3	79.7
4	14.1	2.9	36.1	24.2	3.8	65.8	29.4	8.0	69.0	73.0	14.2	190
5	16.5	3.0	43.5	27.6	6.9	66.8	39.0	9.0	96.8	69.8	29.2	131
Volusia 1	14.8	9.1	18.4	23.6	7.2	52.9	35.2	13.0	71.6	66.9	32.1	112
2	15.7	4.3	36.8	14.8	5.2	31.0	23.7	8.9	47.7	60.4	26.7	109
3	14.5	10.4	13.2	23.5	5.0	60.0	32.7	—	—	74.6	23.1	166
4	15.1	4.3	34.8	19.6	5.0	47.1	24.3	6.5	57.4	46.3	24.7	70.0
Chippewa 1	18.8	8.4	33.5	21.2	7.1	45.4	28.1	13.2	48.1	44.4	57.6	—
2	15.0	4.2	34.8	18.8	6.7	39.0	32.9	8.7	78.0	48.7	43.6	16.5
3	11.3	4.3	22.6	18.1	4.7	43.2	33.9	8.6	81.6	65.1	22.7	137
Kaolinite	7.6	2.6	16	8.5	2.6	19	13.5	5.3	26	13.0	47.2	—
Illite	39.0	19.5	63	44.9	19.3	83	53.0	23.5	95	45.2	25.5	64
Montmorillonite	—	—	—	226	28.0	639	259	30	739	236	8.0	736

TABLE 4
Total potash content of fractionated soil clays and illite

SAMPLE	K ₂ O CONTENT			
	2-1 μ	1-0.5 μ	0.5-0.2 μ	<0.2 μ
	%	%	%	%
Bath 1	3.7	3.8	3.8	3.0
2	3.8	3.9	3.6	3.2
3	4.1	4.6	4.3	2.5
4	5.2	5.9	5.7	4.9
Mardin 1	3.9	4.3	4.0	2.8
2	3.9	4.3	4.0	2.9
3	4.5	5.3	5.1	4.1
4	4.8	5.7	5.8	4.8
5	4.9	6.0	5.9	5.1
Volusia 1	6.3	5.6	5.2	3.5
2	5.6	5.9	5.6	3.8
3	5.4	6.1	5.9	5.7
4	5.6	6.0	5.9	5.0
Chippewa 1	4.1	4.8	4.3	2.1
2	4.5	5.4	6.3	4.3
3	4.7	5.9	6.2	4.8
Illite	4.5	4.9	4.8	4.4

crease with decreasing particle size for all the samples examined. There were no significant changes in exchange capacity either with depth in the profile or among the four soils studied. Samples of chlorite and vermiculite that had been ground to pass a 300-mesh screen were found to have cation-exchange capacities of 10 and 60 me. per 100 gm. respectively.

X-ray data were obtained on samples that represented the extremes in the other measured properties. The major constituents as evidenced by x-ray were illite, other hydrous micas, and chlorite. The amount of chlorite varied in proportion to the 700–850°C. exothermic reaction of the thermal curves. Quartz was found to be limited to the coarse clay, as indicated by differential thermal analy-

TABLE 5
Cation-exchange capacity of fractionated soil and reference clays
In milliequivalents per gram

SAMPLE	CATION-EXCHANGE CAPACITY			
	2–1 μ	1–0.5 μ	0.5–0.2 μ	<0.2 μ
Bath 1.....	15	25	24	47
2.....	16	11	24	25
3.....	12	17	24	39
4.....	11	16	16	40
Mardin 1.....	15	15	20	37
2.....	18	16	26	41
3.....	10	22	20	30
4.....	14	19	28	21
5.....	14	17	24	47
Volusia 1.....	12	16	29	41
2.....	16	9.1	29	26
3.....	15	13	15	42
4.....	14	13	24	36
Chippewa 1.....	20	28	26	28
2.....	12	12	17	31
3.....	6.1	16	16	34
Kaolinite.....	1.3	1.9	3.7	6.3
Illite.....	18	22	31	27
Montmorillonite.....	—	47	86	85

sis. Traces of feldspars were also found in the coarse clay. Again, kaolinite and montmorillonite were not found in appreciable amounts in the soil clays examined.

DISCUSSION

One of the basic assumptions made in identification of minerals in soil clays is that the properties of those minerals are identical with those of a set of reference samples of known mineralogical composition. If such an equivalence of properties exists, it would be possible to establish accurately the mineralogical composition of a soil clay from measurements of as many properties of that clay as there are

mineralogical constituents in it. If it is further assumed that there are no more than three major clay minerals present in the soil clay and that the sum of these three equals 100 per cent, it then becomes possible to estimate mineralogical composition on the basis of two independent sets of measurements of properties.

Since the data indicated that the properties of these soil clays were most like those of illite, an attempt was made to assign quantitatively the properties measured to the illite group. The illite percentages as calculated from the data obtained from differential thermal analysis, ethylene glycol retention, and cation-exchange capacity are shown in table 6. On the thermal curves, the 600°C. endothermic reaction was attributed to illite. The percentage illite was calculated by using the ratio of the peak height of the unknown to that of the reference illite

TABLE 6
Percentage illite in fractionated soils clays calculated from differential thermal, ethylene glycol retention, and cation-exchange capacity data

SAMPLE	FROM DIFFERENTIAL THERMAL				FROM ETHYLENE GLYCOL RETENTION				FROM CATION-EXCHANGE CAPACITY			
	2-1 μ	1-0.5 μ	0.5-0.2 μ	<0.2 μ	2-1 μ	1-0.5 μ	0.5-0.2 μ	<0.2 μ	2-1 μ	1-0.5 μ	0.5-0.2 μ	<0.2 μ
Bath 1.....	53	78	53	75	84	76	52	65	83	100	78	65
2.....	59	86	67	92	69	73	65	65	89	50	78	93
3.....	53	78	67	>100	80	42	80	85	67	78	78	80
4.....	47	86	87	>100	37	49	58	85	61	72	51	75
Mardin 1.....	59	64	67	100	81	63	76	66	83	68	65	80
2.....	53	71	80	91	84	71	66	85	89	72	84	75
3.....	41	86	74	>100	53	53	62	90	58	100	65	100
4.....	47	86	93	>100	57	80	73	65	78	86	90	78
5.....	53	100	80	100	69	81	87	85	78	78	78	65
Volusia 1.....	53	64	87	100	29	64	75	85	67	72	94	75
2.....	47	50	73	>100	58	38	50	85	89	41	94	96
3.....	41	78	87	>100	21	73	—	70	83	59	48	72
4.....	59	71	87	>100	55	57	60	91	78	59	78	80
Chippewa 1.....	41	78	93	33	53	55	51	—	100	90	84	100
2.....	57	85	93	100	55	47	82	26	67	55	55	95
3.....	57	93	>100	>100	36	52	86	85	34	78	51	95

for the corresponding size fraction. In several of the <0.2 μ samples the peak height of the soil clay exceeded that of the reference illite. In all such cases, the presence of a marked endothermic peak in the 650 to 850°C. region indicated that chlorite also was present. Since this mineral also gives an endothermic reaction at 600°C., it would reinforce the illite reaction at that temperature.

For calculations based on ethylene glycol retention, the percentage illite was determined by using the ratio of the internal surface of the soil clay to that of the reference illite in the same size fraction. Again, in the <0.2 μ fractions, it was impossible to assign all the surface to illite. The necessary surface could have been obtained by assuming the presence of montmorillonite to approximately 25 per cent. The differential thermal curves, however, virtually eliminated the pos-

sibility of the presence of montmorillonite in such large amounts. It was not possible to account for the extra surface by assigning it to chlorite, since the internal surface of this mineral is essentially the same as that of illite. It is entirely possible, however, that the chlorite which is present or the illite in these samples has ethylene glycol retention capacities greater than those of the particular reference samples that were examined.

The ratio method was also used to estimate the percentage illite in the soil clays on the basis of cation-exchange capacity. It was again impossible to assign all of the observed exchange capacity to illite if it was assumed that the illite present in the soil clays had the same cation-exchange capacity as the reference sample examined.

If the basic assumptions were valid, the percentages of illite calculated by the three methods would have been in agreement. Table 6 shows that this was not strictly true, although there is a general correspondence between the values calculated from differential thermal analysis, ethylene glycol retention, and cation-exchange capacity. Since there was no logical reason to accept any one of the estimates as the most reliable, an attempt was made to arrive at an integrated

TABLE 7
Average properties for unfractionated reference clays

	K ₂ O	ETHYLENE GLYCOL FOR INTERNAL SWELLING	CATION- EXCHANGE CAPACITY	MEAN INDEX (Y)
	<i>per cent</i>	<i>Δmgm./gm.</i>	<i>me./100 gm.</i>	
Kaolinite.....	0	6	8	2
Illite.....	6	20	25	10
Montmorillonite.....	0	220	80	47

estimate based on several properties. Hendricks and Dyal (4) have suggested that the mineralogical composition of soil clays be designated in terms of a group of indexes such as ethylene glycol retention, total potash content, and exchange capacity rather than expressed as percentage montmorillonite, kaolinite, and illite. This idea has been expanded to arrive at a mean index representing the soil clay. In the calculation of this index the properties of illite were arbitrarily assigned values of 10. The ratio of the corresponding property of kaolinite, montmorillonite, or the soil clay to illite was then calculated and multiplied by 10 to give a numerical index. The mean of the several indexes calculated in this way was then taken as the best estimate of the mineralogical composition of the unknown sample. The average properties used in the calculation of these indexes are listed in table 7, together with the calculated mean indexes, Y, for kaolinite, illite, and montmorillonite. The method of calculating the Y value is illustrated for kaolinite as follows:

$$\frac{1}{3} \left(\frac{0}{6} + \frac{60}{20} + \frac{80}{25} \right) \cong 2$$

Table 7 shows that the three principal clay minerals have widely different Y values. If mineralogical designations are to be given to soil clays for which Y values have been calculated, it is suggested that "kaolinite-like" be used for Y values 0-5, "illite-like" for Y values between 5 and 25, and "montmorillonite-like" for Y values > 25 . Because of uncertainties regarding the hypothesis of equivalence of properties and the presence in soil clays of reactive constituents other than kaolinite, illite, and montmorillonite, unqualified statements regarding the mineralogical composition of soil clays are seldom justified. It is more realistic to describe soil clays in terms of an index such as the Y value or to say that the observed properties of the soil clay are equivalent to those of a certain mixture of the particular clay mineral reference samples that were examined.

TABLE 8

Calculated percentage potash, ethylene glycol retention, cation-exchange capacity, and mean index for total soil clay

SAMPLE	K ₂ O	ETHYLENE GLYCOL FOR INTERNAL SWELLING	CATION- EXCHANGE CAPACITY	MEAN INDEX (Y)
	%	Δ mgm./gm.	me./100 gm.	
Bath 1.....	3.5	27.7	29	10
2.....	3.7	20.9	16	8
3.....	3.8	20.2	22	8
4.....	5.4	17.4	21	9
Mardin 1.....	3.6	16.8	24	8
2.....	3.6	23.5	28	10
3.....	4.6	17.8	21	8
4.....	5.2	32.9	22	11
5.....	5.5	29.5	29	12
Volusia 1.....	5.0	21.0	26	10
2.....	5.3	16.7	19	8
3.....	5.7	—	24	10*
4.....	5.6	16.4	22	8
Chippewa 1.....	3.4		26	9*
2.....	4.9	10.9	19	7
3.....	5.3	23.2	19	9

* Based on two properties only.

It should be emphasized that the Y values should not be used blindly, since they do not represent single-valued combinations of mineral species. For example, it would be possible to have a mixture of kaolinite and montmorillonite with a Y value of 15, which would place it in the range of illite. The absence of potash from such a mixture, however, would indicate that the unknown was not illite.

Y values based on the three properties discussed were calculated for the soil clays and are summarized in table 8. For this purpose, a mean value of each property was calculated for the total clay content of the soil, a weighted average of the fractionated samples based on mechanical analysis being used. The Y values of the soil clays range from 7 to 12. It was concluded that these clays are predominantly "illite-like" and that their properties can be explained by assum-

ing that they contain approximately 75 per cent illite of a type similar to that used as a reference material in these studies.

Although the coarse clay fractions contained small quantities of quartz, none was found in the finer fractions. The x-ray data clearly indicated that the $<1.0 \mu$ clay contained no primary minerals.

The remarkably constant illite content of the four soils, both with regard to depth in the profile and among the profiles, strongly suggests that the clay mineral has been obtained directly from the disintegration of the shale in the parent material. Apparently these soils have not been subjected to sufficient weathering to produce a noticeable advance in the weathering sequence, but reflect mineralogical characteristics that have been inherited from the shaley parent material.

SUMMARY AND CONCLUSIONS

Fractionated clays from soils of a drainage catena of southern New York were examined by the techniques of differential thermal analysis, ethylene glycol retention, total potash content, cation-exchange capacity, and x-ray methods. It is suggested that several properties be combined to give a mean index (Y) which would be used to characterize soil clays. Such a treatment was applied to the data obtained.

The following conclusions were drawn:

The observed properties of most of the soil clays could be explained by assuming that they contained 60–80 per cent illite similar to that of the reference sample of this mineral that was studied.

Chlorite made up an appreciable quantity of many samples.

Lesser amounts of unidentified iron or aluminum oxides were undoubtedly present in the finer fractions.

Quartz not exceeding 10 per cent was found in the $2-1 \mu$ fractions but was not present in the finer clays.

The striking similarity of all the clay fractions examined, with regard to depth in the profile and drainage condition, indicated that these soils have not been subjected to sufficient weathering to alter the original shale inherited from the parent material.

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CLAY MINERALOGY OF RECENT GLACIAL ALLUVIUM SOILS OF WESTERN WASHINGTON

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Received for publication January 8, 1952

Soils derived from recent glacial alluviums in the valleys of western Washington are known to have the ability to fix large amounts of added phosphates. It was thought that this fixation might be linked with the nature of the clay mineral, that is, with the percentage of kaolinite (4). The clay mineralogy of these soils was therefore studied. The soils investigated are important agriculturally, and it was believed that some basic information concerning their chemical and physical character would contribute to a better understanding of their agricultural behavior.

MATERIAL AND METHODS

The soils were collected in the Puyallup River Valley near Puyallup, Pierce County, Washington.² Soil series selected were Pilchuck, Sultan, Puyallup, and Puget. The position of the soil series in relation to one another is shown in figure 1. For this study, three samples of the Sultan and single samples of the others were collected. All samples studied were from the surface 12 inches. All soils were under intensive cultivation except for the Puget, which was in pasture. In general, the Sultan and Puyallup series are the most valuable agricultural land. The Puget is generally poorly drained and fine textured, whereas the Pilchuck is excessively well drained and coarse textured.

After being air-dried, the samples were passed through a 2-mm. sieve and were characterized by the determinations of particle size distribution (7); total and cation exchange capacities (8); pH, by glass electrode; and organic carbon (8).

Silt and clay fractions were obtained for analysis by screening out the sand and by sedimentation to remove the clay in suspension. The clay was dispersed with sodium hexametaphosphate after H_2O_2 treatment for organic matter removal. Clay separates (2.00–0.30, 0.30–0.15, 0.15–0.10, <0.10 μ) were obtained by successive passes of the suspension through a Sharples supercentrifuge at calculated rates of flow (1). The clay divisions were precipitated with N $CaCl_2$, thrown on a filter, washed repeatedly with the $CaCl_2$ solution, and then with 80 per cent ethanol until free from chloride. After drying, the separates were ground to pass a 60-mesh sieve and were stored in a desiccator at a relative humidity of 52 per cent using saturated $Mg(NO_3)_2$ solution.

Differential thermal analyses were performed with a set-up similar to those

¹ Scientific Paper No. 1081, Washington Agricultural Experiment Stations, Pullman, Project No. 871. The author is now with the Division of Soil Survey, U. S. Department of Agriculture.

² F. T. Tremblay, Western Washington Experiment Station, Puyallup, located and helped collect the samples.

found in the literature (3, 9, 10). A linear heating rate of 12.5°C. per minute was maintained. All temperature differences were measured with chrome-alumel thermocouples.

The clay fractions, as prepared for differential thermal analysis, together with the silt and very fine sand fractions were used for x-ray studies. The various fractions were placed as a thin paste on a microscope slide and allowed to dry.³ The paste was prepared with about 0.15 gm. of clay and 12 to 15 drops of a 10 per cent glycerine solution. The x-ray diffraction patterns were obtained with a North American Philips (Norelco) x-ray diffraction unit.⁴ The x-ray equipment was used both with a copper target tube and nickel filter and with an iron target tube and manganese filter. X-ray diffraction intensities were recorded on a Leeds and Northrup recorder activated by a scanning unit consisting of a Geiger tube mounted on a goniometer rotated by an electric motor.

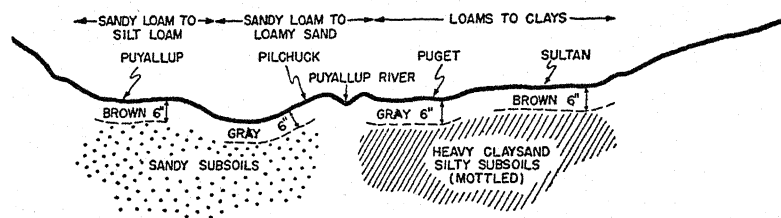


FIG. 1. SCHEMATIC DIAGRAM OF THE RELATIVE POSITION AND NATURE OF THE SOILS SAMPLED After Dr. L. C. Wheeting, professor in soils, State College of Washington.

EXPERIMENTAL RESULTS

Soil characteristics of the six samples are shown in tables 1 and 2. From the data for mechanical analysis and organic carbon, the soils selected for study would appear to be representative of the series named.

Curves of differential thermal analyses for the soils were compared with curves from standard minerals.⁵

The curves showed little indication of the presence of the clay mineral kaolinite. In the samples of Puget, Puyallup, and Pilchuck, the percentage of montmorillonite approached 90 per cent of the $<0.1 \mu$ material, based on magnitude of the thermal peaks, and decreased with a corresponding increase in illite in the coarser fractions. In the Sultan profiles, montmorillonite also occurred in all size fractions, particularly that $<0.10 \mu$. In the Sultan I, illite was estimated at 25 to 50 per cent from the finer to coarser sized fractions. Exothermic peaks around 700°C. in the Pilchuck, Puget, and Puyallup fractions may indicate the presence of some iron minerals, perhaps siderite. Little, if any, indication of the presence of high aluminum minerals, namely, gibbsite or diaspore, was found.

³ According to directions obtained from C. D. Jeffries, Pennsylvania State College.

⁴ X-ray equipment was used through the cooperation of the Department of Physics and the Institute of Technology, The State College of Washington, Pullman.

⁵ The latter were obtained from R. E. Grim and S. B. Hendricks, Illinois Geological Survey and U. S. Department of Agriculture, respectively. Grim has presented differential thermal curves for many of these standard minerals (2, 3) and mixtures thereof.

Irregular peaks in a few of the separates, particularly in the coarser fractions, were an indication—substantiated by laboratory observations—that a considerable portion of these fractions consisted of finely ground minerals ordinarily found in the silt and very fine sand fractions. To the unaided eye, and under low power magnification, the coarser clay fractions appeared similar to those of the silt and very fine sand separates. Only in the $<0.10 \mu$ and to some extent the $0.15\text{--}0.10 \mu$ fractions did the gross physical characteristics appear different from those of the silts and fine sands. It should be noted that only the 0.10μ fraction

TABLE 1

Particle size distribution, organic carbon, and soil reaction of surface samples of alluvial glacial soils from western Washington

SERIES	ORGANIC CARBON	pH		PARTICLE SIZE DISTRIBUTION			
		Saturated paste	Dilution 1:2.5	Sand	Silt	Clay (0.002 mm.)	Texture
	%			%	%	%	
Pilehuck.....	1.1	6.32	6.65	62.36	33.94	3.70	Very fine sandy loam*
Sultan I.....	0.4	6.70	6.80	32.77	62.40	4.83	Silt loam
Sultan II.....	2.8	5.80	6.75	11.87	69.53	18.60	Silt loam
Sultan III.....	2.1	6.08	7.10	2.70	81.91	15.39	Silt loam
Puyallup.....	2.6	6.16	6.25	44.61	47.67	7.72	Loam
Puget.....	3.2	5.82	6.85	2.98	67.93	29.09	Silty clay loam

* U. S. Department of Agriculture Division of Soil Survey, 1950, textural triangle.

TABLE 2

Total exchange capacity and exchangeable cation capacity of surface samples from alluvial glacial soils of western Washington

In me. per 100 gm. soil

SERIES	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE CATIONS			
		Ca	Mg	Na	K
Pilehuck.....	7.04	4.73	0.89	0.12	0.33
Sultan I.....	7.82	5.26	2.00	0.25	0.17
Sultan II.....	16.83	9.30	2.67	0.37	0.36
Sultan III.....	15.84	10.98	5.79	0.30	0.44
Puyallup.....	13.80	8.58	1.35	0.28	0.32
Puget.....	23.26	6.55	9.11	3.64	3.52

appeared lyophilic when CaCl_2 was added to aid in precipitation of the fractions after separation in the supercentrifuge.

These results are augmented by the data in table 3. The increase of the total exchange capacity with increasing fineness of the fraction is obvious. The value of the exchange capacity of the $<0.10 \mu$ fraction is approximately that given in many reports for bentonites or montmorillonites. These exchange capacities would support the contention that the $<0.10 \mu$ samples are largely montmorillonitic and that considerable amounts of illitic and montmorillonitic clays occur in the coarser clay fractions.

With an x-ray spectrometer, patterns for the very fine sand, silt, and four clay fractions of each of the six surface soils were obtained. These patterns were compared with a series of standard clay mineral patterns. Patterns of standard minerals similar to those published by Jeffries (5, 6) were also used for comparison.

The fine sands of all soils, especially the Sultans and Puyallup, appeared to have considerable quartz. The silt fraction, and to a large extent the coarser clay fraction (2.00–0.30 μ), contained a large amount of quartz. There was an indication of micas in the very fine sands and silts, but it was largely submerged by the quartz lines. Otherwise, the patterns gave no particular lead as to the mineralogical content of the samples. In view of the possible presence or absence of the more important clay minerals, the absence of kaolinite peaks was readily noted. The presence of illite was somewhat masked by quartz in the coarser fractions and did not show in the finer fractions. The presence of some members of the mont-

TABLE 3

Total exchange capacities of certain clay fractions obtained from samples of glacial alluvial western Washington soils

SAMPLE	CLAY FRACTION	TOTAL EXCHANGE CAPACITY
	μ	me./100 gm. soil
Sultan II	2.00–0.30	28.7
	0.30–0.15	54.2
	<0.10	91.8
Sultan III	2.00–0.30	24.6
	0.30–0.15	44.4
Puget	2.00–0.30	22.8
	0.30–0.15	47.0
	0.15–0.10	65.4
	<0.10	89.2

morillonitic group of clays was plainly recorded. There was little indication of high iron or aluminum minerals in the patterns traced.

Considerable fluorescence in the patterns of the finer fractions was probably due to iron in the soil samples. Samples had not been treated for removal of free iron oxide. It was feared that such drastic chemical treatment on soils thought to contain appreciable amounts of free iron and aluminum or minerals high in their content, or both, might lead to changes in the soil system beyond mere cleaning up of the more resistant minerals. For these reasons, the previous study did not involve iron removal. The interference of secondary radiation, however, remained a problem.

To overcome this apparent difficulty, the curves for the <0.10 μ fractions were traced, an iron target for radiation source and a manganese filter being used. By such an x-ray arrangement, the interference of free iron oxide was largely eliminated. No kaolinite pattern appeared in the <0.10 μ material. Neither was the occurrence of illite indicated. Only montmorillonite patterns were to be found.

The relationship to the standards indicated that the Puyallup Valley samples might well contain a montmorillonite with considerable substitution of iron in the lattice, because the nontronite curve was closely approximated by the patterns of the fine fractions of the clay.

SUMMARY AND CONCLUSIONS

Six samples of surface soils, representative of the agriculturally valuable land in the Puyallup Valley of western Washington and known to have a relative high phosphate-fixing ability, were collected for the study. They were characterized by determinations of particle size distribution, organic carbon, pH, total exchange capacity, and exchangeable cations. The clay was separated into fractions of 2.00–0.30, 0.30–0.15, 0.15–0.10, and <0.10 μ . Differential thermal curves and x-ray spectrometer patterns were obtained for these clay divisions. X-ray spectrometer patterns were obtained also for the silt and very fine sand fractions.

The samples were collected as representatives of the Pilchuck, Sultan, Puyallup, and Puget soil types as found in Pierce County, Washington. Ionic exchange capacities, differential thermal curves, and x-ray diffraction patterns of the soil fractions studied indicated that the clay mineral content of the finer clay fractions was largely montmorillonite, whereas the coarser clay fraction and the silt and very fine sand were largely quartz, with some illite in the coarse clay. There was little indication of substantial amounts of high Al and Fe minerals. In these soils derived from recent glacial alluvium, the clay mineral kaolinite was not found in amounts exceeding 5 per cent; it would appear not to be a major factor, therefore, in the phosphate fixation.

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RAPID SEMIMICROMETHOD FOR CATION-EXCHANGE CAPACITIES OF CLAYS AND SOILS WITH THE FLAME PHOTOMETER

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Received for publication December 7, 1951

In the course of a study of the clay mineralogy of New Zealand soils, the data obtained by x-ray diffraction and thermal analysis were often considered inadequate. Further evidence was needed. As the order of cation-exchange capacities of the recognized clay minerals was known, it was decided that determinations of cation-exchange capacity would provide valuable checks on analyses of clays by other methods.

Methods described by other workers for exchange capacity require samples weighing 2 or more gm. When the supply of clay is limited to that obtainable from routine sedimentations, use of such large quantities for exchange-capacity determinations restricts the number of other tests that can be carried out. This may explain the absence of exchange capacity data from many publications on clay mineralogy. In many New Zealand soils the clay content is low, sedimentation yielding as little as 0.3 gm. clay from 10 gm. of soil. A method for determining cation-exchange capacity on samples weighing 0.1 gm. or less was required, preferably one with final analysis by the rapid methods of flame photometry.

Rendig (3) described a procedure in which 2 gm. of clay is saturated with potassium ions and the potassium then extracted by centrifuging with a neutral solution of ammonium acetate and magnesium acetate. The potassium content of the extracting solution is determined with a flame photometer. By this method Rendig was able to determine the cation-exchange capacities of four samples in duplicate in 4 to 5 hours.

The procedure described in the present paper eliminates centrifuging and simplifies the nature of the extracting solutions, thereby enabling faster determinations to be made on smaller samples.

Samples were leached in leaching tubes with potassium acetate, then with 95 per cent ethyl alcohol, and finally with ammonium acetate. Potassium in the last solutions was determined with a Beckman flame spectrophotometer.

Because the flame method is very sensitive to sodium ions, sodium acetate was tried in the initial stages of this work in place of potassium acetate. It was found, however, that the results obtained with sodium were not so satisfactory as those obtained with potassium. Sodium contamination from glassware and chemicals caused high and variable blanks, which prevented good duplication of results and made small differences in capacity meaningless.

Potassium contamination as shown by blanks was almost nonexistent. The loss in accuracy of measurement due to the lower relative luminosity of potassium was negligible over the range of concentrations used (0.005 *N*–0.0005 *N*).

A further possibility of error, however, introduced by the use of potassium was that due to fixation. Stanford (5) has shown that electrolyzed illite of less than

2 μ diameter fixed only 1.39 me. of potassium per 100 gm. of clay after standing for 48 hours in a moist condition at a pH of 8.4. Montmorillonite fixed considerably less than this. In the method herein described the potassium acetate leaching took no more than 60 minutes and was immediately followed by subsequent leachings. The amount of fixation under these conditions was negligible.

Although the method was originally developed to determine the cation-exchange capacity of clays, it has been found suitable also for soils. Because of sampling difficulties, duplication of results with soils is not so good as with clays.

EXPERIMENTAL

Small leaching tubes were prepared and provided with filter pads consisting of a layer of glass wool, a layer of filter paper pulp, and a layer of acid-washed silica sand. A 0.1-gm. sample was weighed out, mixed with an equal weight of sand to aid permeation, and introduced into a leaching tube. The sample was then leached successively with 40 ml. of normal potassium acetate (adjusted to pH 7 with glacial acetic acid), 40 ml. of distilled 95 per cent ethyl alcohol,¹ and finally with 40 ml. of normal neutral ammonium acetate. The last leachate was made up

TABLE 1
Depression of potassium luminosity in ammonium acetate solution

POTASSIUM NORMALITY	RELATIVE LUMINOSITY	
	In 0.2 N HCl	In N NH ₄ OA ₂
0.005	100	84.8
0.002	48.0	40.0
0.001	27.2	22.7
0.0005	11.2	11.0

exactly to volume and the potassium content determined with a Beckman model D.U. spectrophotometer with flame attachment (2).

A flame photometric procedure for the determination of cations leached from soils at present in use in this laboratory has been described by Fieldes *et al.* (1). The final flame analysis is made on 0.2 N HCl solutions. It was expected that the use of normal ammonium acetate solutions would cause depression of potassium luminosity. This was borne out, as shown in table 1. In consequence, a series of potassium standards in normal ammonium acetate was prepared and used to construct the curves from which the cation-exchange figures were obtained.

RESULTS

To test the method over as wide a range of capacity as possible, mixtures of kaolinite (McNamee Mine near Langley, South Carolina) and montmorillonite (Yavapai Co., Arizona) were prepared. These mixtures had capacities ranging from 5 to 100 me. per 100 gm. Table 2 shows the results of replicate determinations of the capacities of these mixtures. The right hand column in the table lists capacities obtained by calculations using the experimental values 4.8 and 103 for

¹ Experiments have shown that it is unnecessary to correct the alcohol for acidity.

kaolinite and montmorillonite respectively. Replication to within 10 per cent except in low-capacity kaolinite was not difficult. In all cases, further leachings with ammonium acetate liberated negligible amounts of potassium.

TABLE 2
Cation-exchange capacity of kaolinite-montmorillonite mixtures
In me. per 100 gm.

MIXTURE*	CATION-EXCHANGE CAPACITY						
	Replicate determinations					Average	Calculation
K	4.3	4.0	5.2	5.4	5.0	4.8	4.8
90% K	14.0	14.0	15.0	15.0	14.2	14.4	14.6
10% M							
75% K	29.6	29.4	27.2	32.2	32.0	30.0	29.4
25% M							
70% K	30.8	33.3	36.4	34.8	34.2	33.9	33.3
30% M							
50% K	51.4	53.4	55.0	58.0	56.4	54.8	52.6
50% M							
40% K	59.6	59.4	60.8	60.0	63.8	60.7	63.7
60% M							
25% K	80.0	75.2	78.0	75.8	80.0	77.8	78.6
75% M							
M	102	104	102	102	104	103	103

* K = kaolinite; M = montmorillonite.

TABLE 3
Comparison of cation-exchange capacities obtained by two different methods

SOIL NO.	DESCRIPTION	CAPACITY		CLAY MINERALS
		NH ₄ ⁺	K ⁺	
		me./100 gm.	me./100 gm.	
1440B	Tinopai sandy loam (podzol).	2.5	2.1	Quartz
5117B	Wharekaka sandy loam.....	8.7	8.5	Quartz, halloysite, illite
4846B	Pawson silt loam.....	10.7	11.3	Quartz, illite, feldspars
2079B	Omarama silt loam.....	14.4	10.0	Kaolin, illite, mica
2082A	Alexandra sandy loam.....	21.2	18.4	Illite, feldspars
1603A	Katrine sandy loam.....	28.8	31.0	Montmorillonite, illite
3243A	Oroville sandy loam.....	35.6	38.6	Quartz, allophane, illite
3861B	Parore peaty sandy loam...	90.5	87.3	—
5920D	Clay from Wharekaka sandy loam.....	32.2	32.8	Quartz, montmorillonite, chlorite
5920E	Clay from Wharekaka sandy loam.....	41.2	39.9	Montmorillonite, chlorite

Results of capacity determinations on a set of ten soils and clays by this method and an ammonium acetate method similar to that described by Schollenberger and Simons (4) are listed in table 3. The soils selected represent a wide variety of

types containing a wide range of clay minerals. They include a peat soil (3861B—loss on ignition 76 per cent); the A₂ of a Kauri podzol (1440B); a strongly gleied, yellow-gray earth (5117B); a transitional yellow-gray-yellow-brown earth (4846B); a moderately leached, yellow-brown earth (1603A); a moderately leached, yellow-brown loam (3243A); a weakly leached, brown-gray earth (2082A), and a moderately leached, brown-gray earth (2079B). The last two soils are from low rainfall areas. The two clay samples (5920D and 5920E) were separated from a gleied, yellow-gray earth.²

The agreement between the two sets of results is good, particularly when it is realized that the ammonium acetate estimations were made on 10-gm. samples and the potassium acetate on 0.1-gm. samples. The agreement between the results for the two clay samples is better than that for the soils. This is considered due to the difficulty of sampling soils when only 0.1 gm. is taken.

RAPIDITY OF METHOD

The number of samples that can be analyzed simultaneously is limited only by the quantity of glassware that can be conveniently handled.

For one sample the whole procedure, including the weighing out of the sample, takes about 3½ hours. Each additional sample, however, requires only about 3 minutes. This is the time taken up in weighing out the sample and in obtaining a relative luminosity reading on the flame photometer. Hence the cation-exchange capacities of 24 samples, the number found most convenient in this laboratory, may be estimated in less than 5 hours.

SUMMARY

A method for estimating the cation-exchange capacities of small samples of clays and soils with the flame photometer is described.

As only 0.1 gm. of sample is required, exchange capacities of clays from low clay content soils can be determined without prior time-consuming sedimentations from large quantities of soil.

The method is simple and rapid, the determination of 24 samples being accomplished in less than 5 hours. Good agreement between this and other methods has been obtained. It has already been used extensively by the writers.

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² The soil descriptions are by N. H. Taylor of the Soil Bureau.

PLANT UTILIZATION OF ZINC NUTRIENTS ON HOUSTON BLACK CLAY

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Received for publication January 14, 1952

A comprehensive research program has been undertaken by this institution in an effort to solve the outstanding problems of soil chemistry and fertilizer utilization on Houston black clay of central Texas. In connection with this program, it was imperative to obtain information on the availability of minor element supplements to plants grown on this calcareous soil. In particular, it was essential to obtain concrete evidence regarding the availability to plants of various chemical forms of zinc. Zinc fertilizers labeled with radioactive Zn65 have provided an effective tool for the solution of this problem.

Three sources of zinc, strikingly different in chemical nature, have been tested with two index crops by simple greenhouse pot procedures.

MATERIALS AND METHODS

The three sources of zinc employed in this investigation were $\text{Zn}(\text{NO}_3)_2$, $\text{Zn}(\text{NH}_3)_4(\text{OH})_2$, and Na_2ZnO_2 . All were prepared in this laboratory by simple synthetic methods from radioactive Zn65.¹ In essence, all preparations were achieved through thorough equilibration of the Zn65 and an appropriate amount of nonradioactive $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ prior to chemical conversion. All were employed as aqueous solutions of such concentration that 5.0 ml. was equivalent to 113.6 mgm. of elemental zinc. The fertilizers were intimately mixed with the soil at a rate of 100 pounds of Zn per acre.

Supplementary nutrients were applied as follows: 180 pounds of P_2O_5 per acre as NaH_2PO_4 , 180 pounds of K_2O per acre as KCl , 125 pounds of Mg per acre as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 100 pounds of Esmine¹ per acre, and 175 pounds of N per acre as $(\text{NH}_4)_2\text{SO}_4$ corrected for the nitrogen content of the zinc fertilizer.

Houston black clay, utilized in this study, has been described elsewhere (3). The experimental procedures and greenhouse techniques suitable for radiochemical research have been outlined by numerous workers (4-16). Ryegrass and crimson clover were used as index crops for all three zinc sources. The clover was harvested after 90 days; the ryegrass was clipped twice, 60 days and 90 days after seeding. Plant tissue samples were collected, dried, and solubilized by digestion with nitric and perchloric acids.

Uptake of zinc fertilizer was determined by radiochemical assay of the plant digestates. With only slight modification, the method of Anderson (1), involving the precipitation of zinc as anthranilate, was found to be suitable for this purpose. Nonradioactive $\text{Zn}(\text{NO}_3)_2$ (4 mgm. Zn per 25 ml.) was added as scavenger to

¹ The Zn 65 was obtained from the Isotopes Division, U. S. Atomic Energy Commission.

ensure maximum precipitation. Even under these conditions, only 92.3 per cent average recovery was attained on samples of known composition, and a corresponding correction factor was employed in all subsequent assays. In addition, the radiation characteristics of Zn65 (positron, K-capture, and weak gamma emission) necessitated a self-absorption correction for these assay samples.

RESULTS

The availability of the three zinc sources to the two index crops on Houston black clay is summarized in table 1. All results represent average values from three replicates.

This study, though somewhat limited in scope, revealed certain interesting facts. It showed that all zinc sources tested are readily available to the index crops employed. Further, it showed that there is relatively little difference in availability between sources despite their chemical dissimilarity; that is, divalent cationic zinc, Zn^{++} ; the cationic complex, $Zn(NH_3)_4^{++}$; and anionic zinc, ZnO_2^- , have all been utilized by the plants. For both index crops, $Zn(NH_3)_4(OH)_2$ ap-

TABLE 1
Utilization of various zinc sources by crimson clover and ryegrass on Houston black clay

ZINC SOURCE	ZINC IN PLANT TISSUE DERIVED FROM FERTILIZER		
	Crimson clover 90-day harvest	Ryegrass	
		60-day harvest	90-day harvest
	ppm.*	ppm.*	ppm.*
$Zn(NO_3)_2$	58	38	27
$Zn(NH_3)_4(OH)_2$	76	48	30
Na_2ZnO_2	64	43	33

* Dry-weight basis.

peared to be very slightly more available and Na_2ZnO_2 seemed to be more readily utilized than $Zn(NO_3)_2$. In all cases, however, all sources at this application rate provided an adequate amount of this essential nutrient for normal plant development.

Two points appear worthy of note in connection with this research: despite the high application rate, no zinc toxicity to the plants was observed; further, no evidence of irradiation damage was apparent.

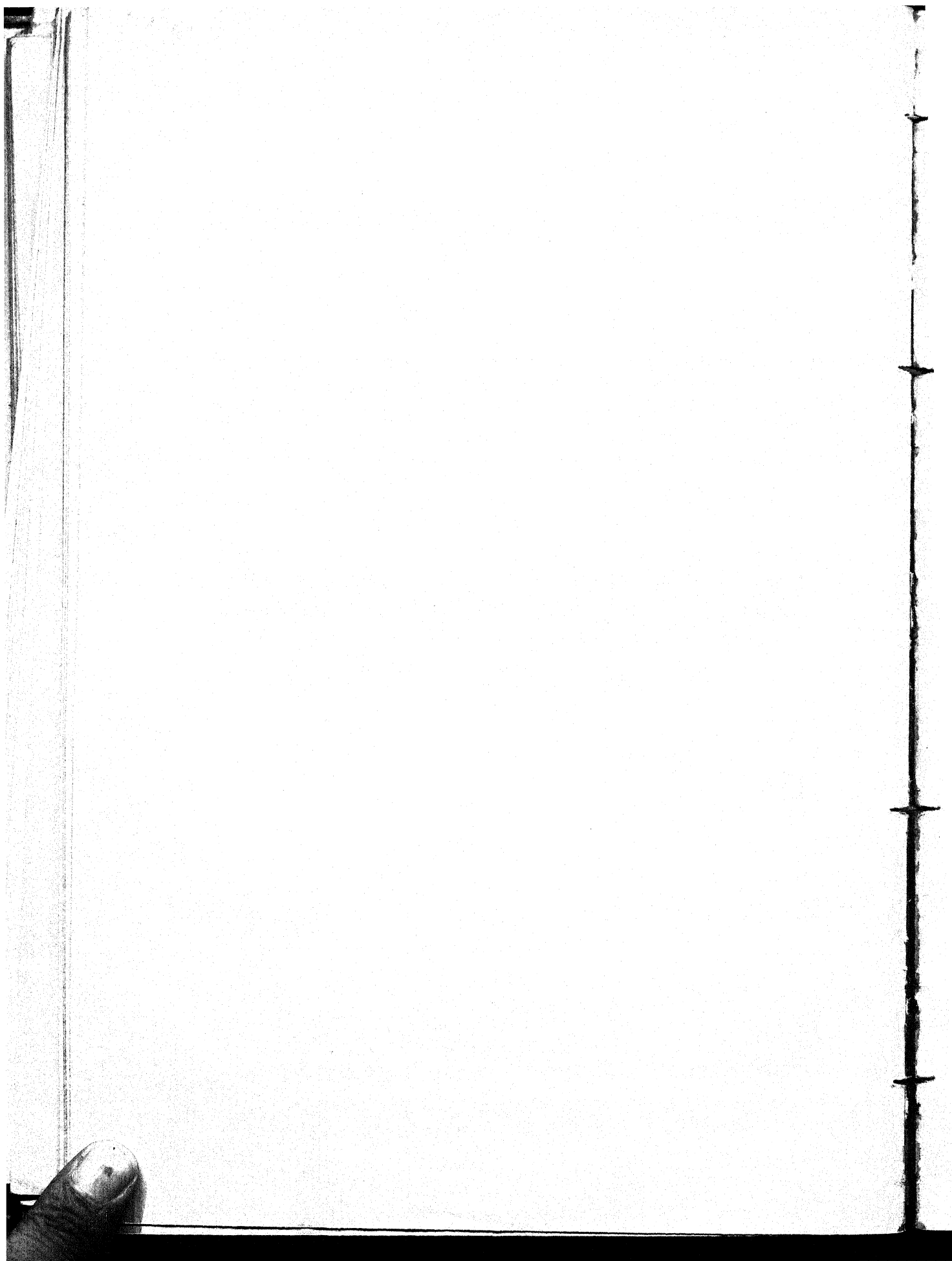
SUMMARY

Zinc nitrate, zinc ammonium hydroxide, and sodium zincate were shown to be readily available to crimson clover and ryegrass grown on Houston black clay. These sources, though markedly different in chemical nature, were almost equally available to the index crops employed.

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POTASSIUM, CALCIUM, AND MAGNESIUM IN TUNG LEAVES AS RELATED TO THESE IONS IN THE SOIL

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Received for publication November 28, 1951

The important role that plant analysis plays in the interpretation of mineral nutrition studies is well indicated in recent reviews of the subject (6, 15). In tung investigations leaf analysis has proved a very useful aid in diagnosing mineral deficiencies and in interpreting the results of both field and sand-culture experiments (2, 3, 4, 13, 14). Leaf analysis has been helpful also as a guide for fertilizer recommendations. A table based on experiments and observations correlated with analyses of several thousand leaf samples has been prepared. It gives the tentative optimum and deficiency ranges in the percentage of mineral elements in tung leaves (9). There is still much to be done in examining more closely the relations of leaf composition to growth and production under field conditions. This work is in progress and will be reported later.

It is well recognized that leaf analysis has its limitations. It yields important information on the nutritional status of the plant at the time of sampling and represents the resultant of a number of factors that have influenced leaf composition. Though leaf analysis may be used to diagnose a mineral deficiency, for example, it cannot answer the question of what caused the deficiency. For this answer it is necessary to investigate the environmental factors, one of the most important of which is the soil.

Much attention has been given in recent years to the effect of the concentration of cations in the soil on the uptake of nutrients by the plant. Some progress has been made in formulating mathematical expressions for this relation (7, 8, 10). Most of this work has been done with annual crops in the greenhouse. Not much information is available on leaf composition and soil interrelations for tree crops, especially under field conditions. The purpose of this paper is to report on a field survey in which an attempt was made to correlate analyses of tung leaves with the exchangeable cations in the soil at the time the leaves were collected.

MATERIALS AND METHODS

During August 1946, 1947, and 1948 midshoot leaf samples were collected from bearing tung trees in various field experiments in different parts of the Tung Belt, together with soil samples from under the trees at the same locations. From these, 51 representative samples were selected to cover the range in soil types on which much of the tung acreage is planted. The soils sampled include those of the Norfolk, Ruston, Ora, Pheba, Red Bay, Arredondo, Lakeland, and Blanton series in Louisiana, Mississippi, or Florida.

The soil samples were taken with a spade at depths of 0 to 6, 6 to 12, and 12 to 18 inches from at least four places under the spread of the branches of each tree from which a leaf sample was taken. Leaf samples from all the trees in a plot

were composited, as were the soil samples from a given depth. Usually there were six or more trees in a plot.

Potassium was determined on a dilute HCl solution of the leaf ash by the cobaltinitrite procedure with ceric sulfate as the oxidizing agent, magnesium by a thiazol yellow method (5), and calcium by precipitation as the oxalate and titration with standard KMnO_4 . Exchangeable potassium, calcium, and magnesium were determined by suitable modifications of the methods used for the leaf analyses, neutral normal ammonium acetate being used for leaching the soils (12). The exchange capacity was determined from the ammonium distillate after replacement of NH_4^+ by acidified NaCl (12).

RESULTS AND DISCUSSION

The ranges in composition of the leaves and soils are given in table 1. These cover values from the lower to upper limits that are ordinarily found in commercial tung orchards.

TABLE 1

*Range in cation content of 51 samples of tung leaves and range of exchangeable cations and exchange capacity of the soils in which the trees were growing**

In milliequivalents per 100 gm.

CATION	ELEMENT IN LEAF DRY MATTER	EXCHANGEABLE CATION IN OVEN-DRY SOIL FROM INDICATED DEPTH		
		0-6 inches	6-12 inches	12-18 inches
K.....	6.4 to 27.9	0.07 to 0.48	0.04 to 0.44	0.02 to 0.46
Ca.....	49.0 to 209.0	0.40 to 4.19	0.20 to 1.99	0.14 to 1.50
Mg.....	15.8 to 56.0	0.10 to 0.91	0.07 to 0.64	0.05 to 0.92
Exchange capacity.....		2.4 to 10.3	2.2 to 8.4	1.2 to 9.8

* Samples collected in 1946, 1947, and 1948 in tung orchards in Florida, Mississippi, and Louisiana.

Correlation coefficients were calculated between the leaf contents of potassium, calcium, and magnesium and the exchangeable cations in the soil. They are given in table 2. The calculations were made with the assumption that the correlations were linear. Graphs plotted from the data show that the relations are largely linear over the range of values obtained in this study. Some representative scatter diagrams are given in figure 1. Probably over a greater range, the relation would be more definitely curvilinear, as found by Van Itallie (7).

There was no significant correlation between leaf potassium and the content of exchangeable potassium in the soil. The scatter diagram in figure 1A illustrates this graphically. When the soil potassium was calculated in terms of percentage of saturation of the exchange capacity, however, a highly significant correlation was obtained between leaf potassium and soil potassium at both 0 to 6 inches and 0 to 18 inches. This is shown graphically in figure 1B. In a previous study with various treatments on one soil type in one location, a highly significant correlation was obtained between leaf potassium and milliequivalents of ex-

changeable potassium (11). It would appear that when soil conditions are fairly uniform the milliequivalents of exchangeable potassium in the soil may be correlated with leaf potassium. When there is a wide variation in soil it is necessary to take into consideration the relation of the exchangeable potassium to the other cations in the soil. That the calcium and the magnesium in the soil are important in this respect is indicated by the highly significant correlation of leaf potassium with the ratio of exchangeable potassium to exchangeable calcium plus magnesium.

A highly significant correlation was observed between the leaf calcium and the milliequivalents of exchangeable calcium in the soil. The correlation was even

TABLE 2

Correlation between content of potassium, calcium, and magnesium in tung leaves and the same cations in the soil under the trees

ELEMENT IN LEAVES	SOIL			CORRELATION COEFFICIENT (r)
	Element or element ratio	Determination	Depth	
<i>me./100 gm.</i>			<i>inches</i>	
K.....	K	me./100 gm.	0-6	+ .14
K.....	K	% saturation	0-6	+ .41**
K.....	K	% saturation	0-18	+ .44**
K.....	K			
K.....	Ca + Mg	ratio of me. values	0-6	+ .44**
Ca.....	Ca	me./100 gm.	0-6	+ .41**
Ca.....	Ca	% saturation	0-6	+ .65**
Ca.....	Ca	% saturation	0-18	+ .63**
Ca.....	Ca			
Ca.....	K + Mg	ratio of me. values	0-6	+ .72***
Mg.....	Mg	me./100 gm.	0-6	+ .15
Mg.....	Mg	% saturation	0-6	+ .03
Mg.....	Mg	% saturation	0-18	+ .20
Mg < 29.....	Mg	% saturation	0-18	+ .63**
Mg.....	K	% saturation	0-6	- .36**
K + Ca + Mg.....	K + Ca + Mg	% saturation	0-6	+ .42**

** Significant at 0.01 level.

*** Significant at 0.001 level.

higher when the exchangeable calcium was calculated on a percentage saturation basis. The difference, however, did not attain statistical significance. The correlation of leaf calcium with percentage of saturation of exchangeable calcium at 0-18 inches was about the same as with that at 0-6 inches. The influence of the exchangeable potassium and magnesium in the soil on the calcium content of the leaves is shown by the very highly statistically significant coefficient of +0.720 for the correlation between leaf calcium and the ratio of calcium to potassium plus magnesium in the soil. This is illustrated graphically in figure 1C. There is some suggestion of curvilinearity in this graph. Calculations were made for curvilinear regression, but it was found that the deviation from linearity was not statistically significant at the 0.05 level.

Magnesium presents a different picture. Leaf magnesium was not significantly correlated with either exchangeable magnesium or percentage saturation of magnesium. It was postulated that for those leaf samples containing magnesium in the suboptimum range (<29 me./100 gm.) soil magnesium may have a

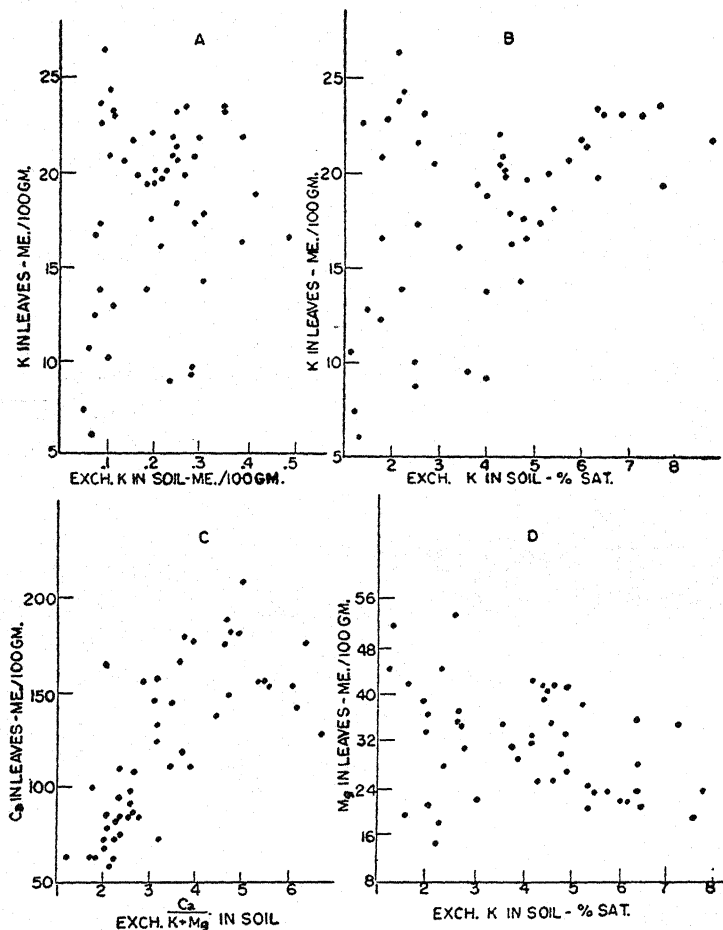


FIG. 1. REPRESENTATIVE SCATTER DIAGRAMS SHOWING RELATIONS BETWEEN CATIONS IN TUNG LEAVES AND THOSE IN THE SOIL

- A. K in the leaves and me./100 gm. of exchangeable K in the soil.
- B. K in the leaves and percentage saturation of exchangeable K in the soil.
- C. Ca in the leaves and $\frac{Ca}{K+Mg}$ in the soil.
- D. Mg in the leaves and percentage saturation of K in the soil.

greater effect on leaf magnesium than when the leaf concentration is higher and the soil magnesium supply may be more than ample. As the correlation between leaf magnesium and degree of magnesium saturation was somewhat higher for the soil to 18-inch depth than for soil to the 0-6-inch depth, the correlation at the

0-18-inch depth with leaf magnesium was determined for the suboptimum samples. A highly significant positive correlation coefficient of 0.63 was found for the 18 pairs of samples in which the leaf magnesium was less than 29 me./100 gm. It is apparent from this calculation that the magnesium supply in the soil was a greater factor in affecting the magnesium content of these leaf samples than of the entire series of 51 samples.

In addition, there is a highly significant negative correlation between leaf magnesium and the percentage of saturation for potassium in the soil (fig. 1D), which indicates that the concentration of potassium in the soil is a much more important factor in the uptake of magnesium by the tree than is the concentration of magnesium in the soil. This is of considerable importance in fertilizer practice in magnesium-deficient areas. Difficulty has been encountered in correcting magnesium deficiency by the application of soluble magnesium salts to the soil. These data would indicate that more consideration must be given to potassium fertilization in controlling magnesium deficiency.

The cation summation values calculated for the leaf samples used in this study failed to show any cation equivalency. Values ranged from 102 to 273 me. per 100 gm. Though sodium was not determined in this study, the amount of this element usually found in tung leaves is so small, in the order of 0.4 me. per 100 gm., that it could hardly be a factor. The probability that the total degree of base saturation influences the total quantity of cations in the leaf tissue is shown by the highly significant correlation of +0.42 between the summation percentage of bases in the soil at the 0-6-inch depth and the cation summation values in the leaves. This, however, would account for only $(0.42)^2 \times 100$, or 17.6 per cent of the relation found.

It is realized that, although some of the correlations are highly significant, they are still not high enough for a satisfactory interpretation, because other factors in the soil beside the potassium, calcium, and magnesium concentrations are operating. The nature of the soil-colloidal complex is important, as has been pointed out (1, 10). The physical properties of the soil affecting aeration and drainage must be considered. The growth and production of the trees are important factors. In continuing this study an attempt will be made to isolate the various factors affecting the relation of the mineral elements in the soil to nutrient content of tung leaves.

SUMMARY

An attempt was made to relate the potassium, calcium, and magnesium contents of tung leaves to the same elements found in the soil under the trees when the leaf sample were taken. Coefficients were calculated for 51 pairs of samples taken from a wide range of different soil types to find the degree of correlation between tung-leaf contents of potassium, calcium, and magnesium and soil contents of exchangeable potassium, calcium, and magnesium. Leaf potassium was not significantly correlated with milliequivalents of potassium in the soil but was highly significantly correlated with the percentage of saturation of potassium in the soil. The correlation coefficient for the 0-6-inch soil level was about the

same as that for the 0-18-inch level. Leaf calcium was highly significantly correlated with milliequivalents of calcium in the soil, and the correlation with the degree of saturation of calcium was even greater, but the increase did not attain statistical significance. The coefficient, $+0.72$, for correlation between leaf calcium and the ratio of calcium to potassium plus magnesium in the soil had very high statistical significance. For the entire series of samples, leaf magnesium was not significantly correlated with soil magnesium on the basis of either milliequivalents or percentage of saturation. For the leaf samples in which the magnesium was less than 29 me./100 gm., however, a highly significant correlation was found with the degree of magnesium saturation of the soil. Leaf magnesium was negatively correlated to a highly significant degree with the percentage saturation of potassium in the soil.

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POTASSIUM-SUPPLYING POWER OF EIGHT ALABAMA SOILS

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Received for publication December 11, 1951

Most of the soils of the southern humid region of the United States have been highly weathered and leached; consequently they are low in both total and exchangeable potassium. There are wide differences, however, in their capacity to furnish potassium for plant growth, as demonstrated by marked variations in response to potassium fertilization. A more precise characterization of typical soils of the area with respect to potassium-supplying power and its relation to measurable soil properties would be helpful in the interpretation of observed responses and the prediction of need for potassium applications.

Earlier investigations of the problem, as well as the experience of farmers and agronomists in general, have indicated that continuous cropping of soils of the region without addition of potassium soon results in depletion of the soil potassium to the extent that satisfactory plant growth can no longer be made.

The literature on potassium release was recently reviewed comprehensively by Reitemeier (9). Wide variation has been found (3, 4, 8, 10) in the number of times a soil must be cropped to exhaust it, but no generally accepted relationship has been established between the potassium-supplying capacity of soils and other soil properties. Reitemeier and co-workers (8) and Ayres (1) reported that the rate of solution of potassium during electrodialysis of a soil is related to the quantities converted from nonexchangeable to readily available form during cropping. Rouse and Bertramson (10) found that for 23 Indiana soils the non-exchangeable potassium extracted by a boiling nitric acid treatment was closely related to the potassium-supplying power of these soils as measured by cropping. Data reported by Hoover and associates (5) indicate that the type and quantity of potassium-bearing clay mineral may have some influence upon the rate of supply of potassium, but sufficient evidence is not available to warrant a definite conclusion.

The purpose of the present investigation was to study the transformations of potassium in certain agriculturally important soils in the southeastern United States in an effort to determine what properties of these soils influence their capacity to convert nonexchangeable potassium to forms readily absorbed by plants.

MATERIALS AND METHODS

Soils used

Eight soils were selected to cover a wide range in chemical and mineralogical properties. They occur in the Coastal Plain, Appalachian Plateau, Piedmont,

¹ A joint contribution from the agronomy department, Alabama Agricultural Experiment Station, and the Bureau of Plant Industry, Soils, and Agricultural Engineering. The author, now senior soil scientist, U. S. Department of Agriculture, was formerly soil chemist, Alabama Agricultural Experiment Station.

TABLE 1
Some chemical and mineralogical properties of eight Alabama soils

SOIL	SEPARATE	FRACTION OF TOTAL SOIL	TOTAL K CONTENT	CHARACTERISTICS OF CLAY SEPARATE				
				Cation- exchange capacity	Kaoli- nite	Mont- moril- lonite	Quartz	Hy- drous mica
		%	ppm.	me./100 gm.	%	%	%	%
Orangeburg sandy loam	Clay	9.8	5,000	26	25	0	30	8
	Silt	25.1	4,700					
	Sand	65.1	140					
	Total soil	—	1,763					
Norfolk sandy loam	Clay	3.0	2,300	32	25	0	45	4
	Silt	6.3	3,500					
	Sand	90.7	70					
	Total soil	—	355					
Susquehanna sandy loam	Clay	15.1	3,300	39	15	15	55	6
	Silt	21.5	2,500					
	Sand	63.4	1,160					
	Total soil	—	1,775					
Cecil sandy loam	Clay	5.6	4,700	25	45	0	30	8
	Silt	10.1	9,500					
	Sand	84.3	2,030					
	Total soil	—	2,934					
Davidson clay loam	Clay	24.8	8,700	31	40	0	15	14
	Silt	23.8	17,400					
	Sand	51.4	2,980					
	Total soil	—	7,831					
Sumter clay	Clay	27.4	4,900	—	—	—	—	8
	Silt	18.3	6,700					
	Sand	18.3	3,540					
	Total soil	*	3,223					
Eutaw clay	Clay	50.8	4,000	68	45	45	10	7
	Silt	28.7	2,600					
	Sand	20.5	2,000					
	Total soil	—	3,141					
Hartsells fine sandy loam	Clay	5.9	8,200	38	15	0	60	14
	Silt	27.6	6,200					
	Sand	66.5	440					
	Total soil	—	2,490					

* Contains about 35 per cent free CaCO_3 .

and Black Belt physiographic regions and were taken from field plots that have had little or no potassium added during the last 20 years. The soil types, together with some chemical and mineralogical data, are listed in table 1. Exchangeable

potassium and total potassium vary widely, as does the predominant clay mineral type. The Hartsells with approximately 15 per cent kaolinite, no montmorillonite, 60 per cent quartz, and 14 per cent hydrous mica is one extreme, and the Eutaw with about 45 per cent each of kaolinite and montmorillonite, 10 per cent quartz, and 7 per cent hydrous mica is the other. It should be pointed out that the method used for quantitative estimation of the various mineral fractions permit an approximation of summation percentages no closer than ± 10 per cent.

The distribution of total potassium among particle size separates of the soils is also shown in table 1. There are wide differences in the composition of the various separates with respect to potassium.

Analytical procedures

Exchangeable potassium was removed by leaching with neutral normal ammonium acetate, and total soil potassium by HF digestion. Potassium in the extracts was determined with a Perkin-Elmer flame photometer. Mineralogical characterization of the clay separates was accomplished by x-ray diffraction (2, 6) and differential thermal (7) methods. Hydrous mica content was calculated from the total potassium content of the clay separates, based on 6 per cent as the average potassium content of hydrous mica. The cation-exchange capacity of the clay separates was determined at pH 6.8 with *N* calcium acetate as the saturating solution.

Plant material was dry-ashed, dissolved in 5 per cent acetic acid, and the potassium content measured with the Perkin-Elmer flame photometer.

Potassium-fixing capacity and release of fixed potassium

One-hundred-gram samples of soil were treated with 360 ppm. of K as KCl, dried once at 70°, and the excess and exchangeable potassium removed by washing with *N* calcium acetate then with water. For 40 days these samples were electrodyalyzed simultaneously with samples of untreated soil, from which exchangeable potassium had been removed in the same way. The difference between the two sets of values thus obtained represents the rate of conversion of fixed potassium to soluble form.

Electrodialysis

One hundred grams of soil was electrodyalyzed for extended periods at a potential difference of 110 volts, cellophane membranes and platinum gauze electrodes spaced 2 inches apart being used. The potassium removed from the soil was determined at appropriate intervals with the flame photometer.

Cropping

Bulk samples of each of the eight soils were screened, thoroughly mixed, and placed in four 2-gallon pots. They were then exhaustively cropped in the greenhouse without additions of potassium. Five crops were grown: sudan grass, turnips, sunflowers, and two crops of peanuts. The soils were not repotted or allowed to dry except between the third and fourth crops.

DISCUSSION OF RESULTS

Release of native nonexchangeable potassium

In the exhaustive cropping study in the greenhouse, potassium-deficiency symptoms were evident in three of the soils by the third crop, and little or no growth was made by the fifth crop except on the Davidson, Sumter, and Eutaw soils. This was undoubtedly due to the exhaustive cropping that the other five soils had undergone in the field prior to the experiment. The amounts of potassium converted from nonexchangeable to exchangeable form during this period of cropping is shown in table 2. No nonexchangeable potassium was released by two of the soils, virtually none by two, and relatively high quantities by four.

TABLE 2

Conversion of potassium from nonexchangeable form in eight soils under continuous cropping in the greenhouse

SOIL	ORIGINAL EXCHANGEABLE K	K REMOVED IN 5 CROPS	EXCHANGEABLE K AFTER 5 CROPS	K CONVERTED FROM NONEX- CHANGEABLE TO AVAILABLE FORM
	ppm.	ppm.	ppm.	ppm.
Orangeburg sandy loam.....	43	41	17	15
Norfolk sandy loam.....	22	17	7	2
Susquehanna sandy loam.....	89	66	18	-5
Cecil sandy loam.....	37	35	8	6
Davidson clay loam.....	89	79	25	15
Sumter clay.....	117	118	41	42
Eutaw clay.....	109	81	26	-2
Hartsells fine sandy loam*.....	24	32	11	19

* Only two crops grown in the greenhouse to date. This soil was cropped for 16 years in the field with no potassium fertilization.

In the Davidson, Sumter, and Hartsells soils, an amount of potassium equivalent to 20 to 60 per cent of that absorbed by the plant was released from originally nonexchangeable form. The data in tables 1 and 2 reveal no relationship between the capacity of the soils to convert nonexchangeable potassium to available form and the original total or exchangeable potassium content of the soil or its distribution according to particle size. There is some indication, however, that the hydrous mica content of the clay may influence the rate of release. It is evident that the degree of weathering and the resulting variation in solubility of the remaining potassium overshadow the effect of variations in the total amount of the element present in these soils.

Further examination of these data reveals that, although there is no relationship between exchangeable potassium and the amount of that element released from nonexchangeable form, a close relationship does exist between the original exchangeable potassium content of the soils and the total potassium absorbed by the five crops. This relationship, shown graphically in figure 1, would be

expected in soils of low potassium-supplying power that have been exhaustively cropped, and lends credence to the concept of exchangeable potassium as an index to the over-all availability of that element during a growing season in soils such as these.

Previously reported investigations (1, 8) have indicated that the rate at which potassium is removed from soil during electro dialysis is related to the quantities converted from nonexchangeable to readily available form during cropping. To determine whether such a relationship exists in the soils included in this study,

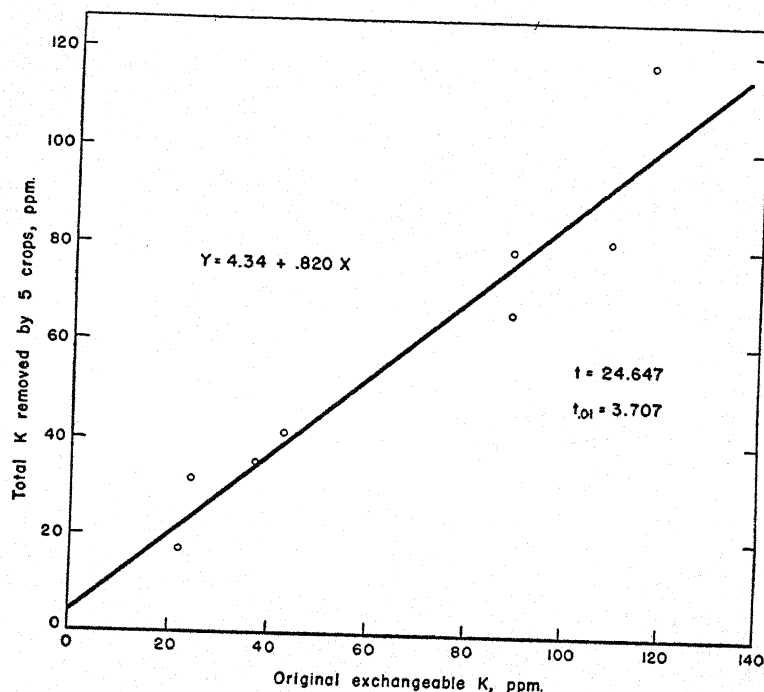


FIG. 1. RELATIONSHIP BETWEEN THE ORIGINAL EXCHANGEABLE POTASSIUM CONTENT OF EIGHT ALABAMA SOILS AND THE AMOUNTS REMOVED BY FIVE CROPS GROWN IN THE GREENHOUSE.

samples taken after the final crop were subjected to electro dialysis for 40 days. The results are shown graphically in figure 2. In general, the amount of potassium removed in 24 hours was about equal to that present in exchangeable form at the beginning of dialysis. The family of curves produced by the treatment of these soils are, with one exception, very similar except for their vertical displacement, which is a result of differences in easily soluble potassium. After 2 to 5 days, the rate of release in all but the Davidson soil had become approximately constant. The Davidson, however, required about 20 days to reach equilibrium, which indicates a marked difference between it and the other soils with respect to the type and amount of potassium-bearing clay minerals. The Davidson clay separate has twice as much hydrous mica as any of the other soils except the Hartsells,

which, however, contains only one fourth as much $< 2 \mu$ material as does the Davidson.

Release of fixed potassium

Six of the soils were selected for a study of potassium-fixing capacity and rate of release of fixed potassium. With the procedure used, the amounts of the added potassium fixed ranged only from 195 ppm. in the Norfolk to 340 in the Sumter, but, as shown in figure 3, the percentage of fixed potassium released upon elec-

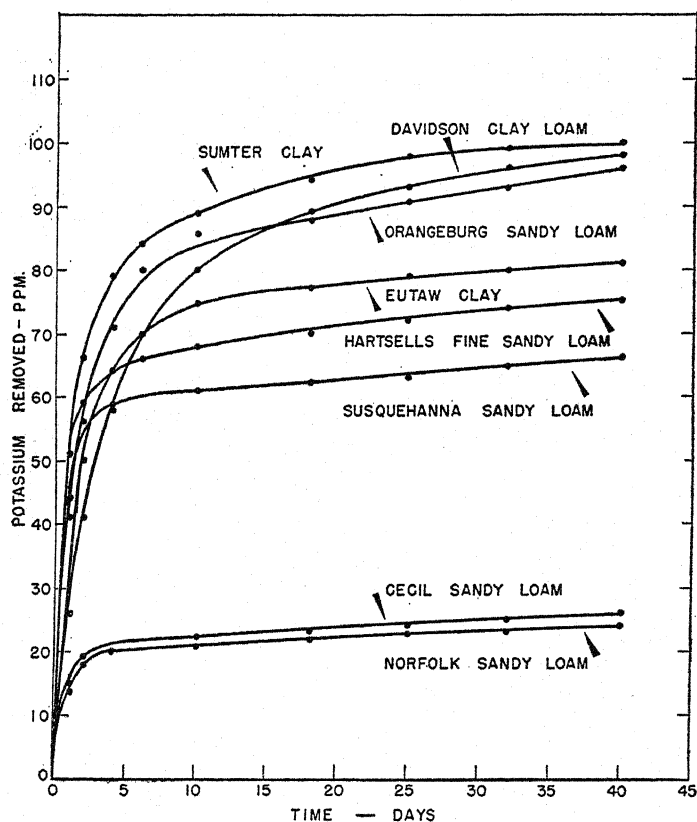


FIG. 2. RATE OF SOLUTION OF POTASSIUM FROM EIGHT ALABAMA SOILS BY ELECTRODIALYSIS

tro dialysis varied widely. In general, it was found that the soils containing montmorillonite fixed larger quantities of potassium than did the kaolinitic soils. The same trend is evident in the release of fixed potassium, both in total amount and percentage of the amount fixed. Further, there is a marked difference in the slope of the release curves following solution of the readily removable portion of the fixed potassium. The kaolinitic soils showed virtually no release beyond this point, whereas the Eutaw and Susquehanna continued to release potassium at a considerable rate. The Sumter cannot be considered in the same

category as the other montmorillonitic soils because of its high content of CaCO_3 . These data strongly suggest that soils of the region containing 2:1 type clay minerals can be expected to fix larger amounts of added potassium than do those predominantly of the 1:1 type, but that they probably will also release a much larger percentage of it to forms available to plants.

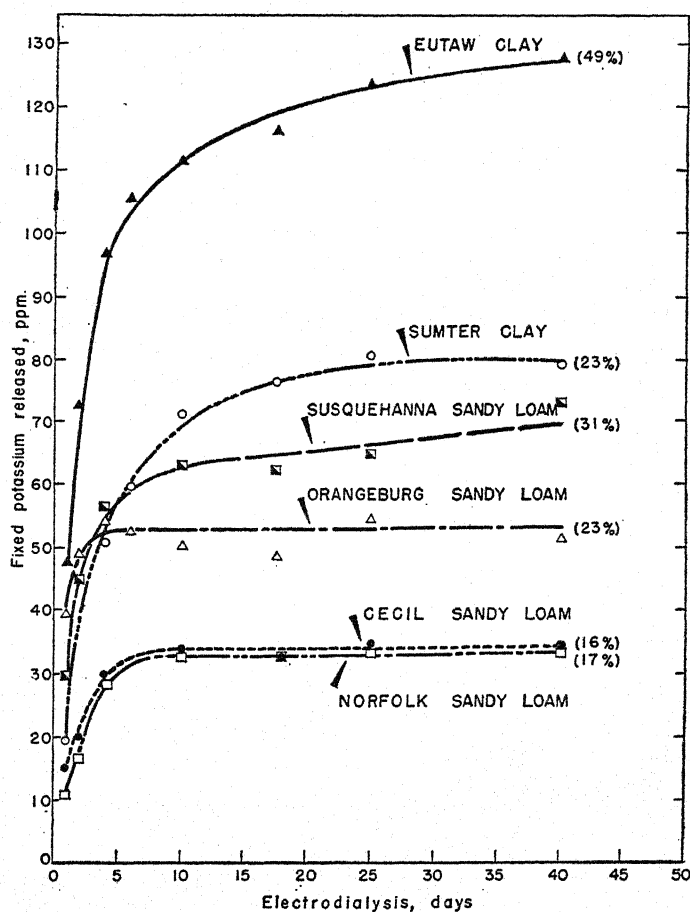


FIG. 3. RATE OF SOLUTION AND PERCENTAGE OF FIXED POTASSIUM RELEASED FROM SIX ALABAMA SOILS BY ELECTRODIALYSIS

Samples of Hartsells soil were taken from a field experiment that provided a wide range of cumulative potassium additions over 18 years and analyzed for exchangeable and electrodialyzable potassium in an effort to determine whether field additions can affect the equilibrium rate of release of potassium. The results of this study are presented in figure 4. Calculations show that the exchangeable potassium in the soils from each of these treatments amounts to 0.8 of that represented by the point where rate of solution becomes essentially constant.

Thus, there is an increasing quantity of relatively soluble nonexchangeable potassium as the annual field additions are increased from 0 to 96 pounds of K_2O per acre. These data show that there has been a measurable build-up of fixed potassium under field conditions even in a coarse-textured soil and that this fixed potassium is definitely more soluble than that contained in the native soil minerals.

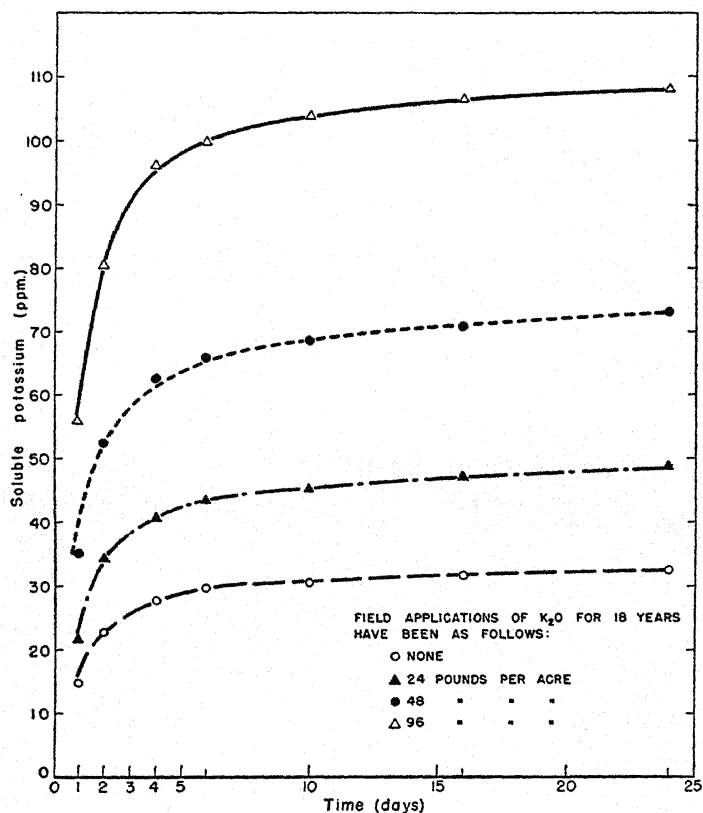


FIG. 4. EFFECT OF POTASH FERTILIZATION ON THE RATE OF REMOVAL OF POTASSIUM FROM HARTSELLS FINE SANDY LOAM BY ELECTRODIALYSIS

SUMMARY

Eight agriculturally important soils representing four physiographic regions and a wide range in chemical and mineralogical composition have been investigated from the standpoint of the transitions of potassium that occur between the exchangeable and nonexchangeable forms. The following tentative conclusions can be drawn:

Considerable variation exists between the soils studied with respect to their rate of release of potassium from mineral forms.

There was no apparent relationship between the capacity of the soils to release

potassium from nonexchangeable forms and either the total potassium content or its distribution among the particle size separates.

There was no relationship between potassium release and the original exchangeable potassium content, but the latter was the chief factor determining the total amounts of potassium absorbed by five crops grown in the greenhouse.

Under some conditions field-applied potassium may accumulate in significant quantities even in coarse-textured soils.

There is a wide range in the tenacity with which applied potassium is retained by the different soils against solution. Of the soils included in this study, those containing montmorillonite released fixed potassium more readily than did the kaolinitic soils.

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NITROGEN GAS FORMATION BY INTERACTION OF NITRITES AND AMINO ACIDS

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Received for publication February 6, 1952

The possibility that nitrites can react with amino acids and ammonia to form nitrogen gas in soils and plants has been emphasized by several workers mentioned in previous publications (1, 2, 3) from this laboratory. Doubtless one of the main reasons for this view is the fact that this reaction occurs so rapidly and completely in the Van Slyke apparatus. In this apparatus the added amino acid commonly reacts with a large excess of NaNO_2 in presence of glacial acetic acid and in an atmosphere of NO , which retards the decomposition of the nitrite.

In our previous work (1, 2) no evidence was obtained to indicate that the nitrite-amino-acid reaction is responsible for any appreciable loss of gaseous nitrogen from green plants. Likewise, Jones (4), using tracer techniques, found no evidence of the reaction in soils. In another publication (3), reporting studies conducted in an atmosphere of air in buffered solutions, using Warburg vessels, it was observed that nitrous acid reacts to a limited extent with alanine to form nitrogen gas at pH values of 4.5 and lower. Where NaNO_2 was added at a concentration of 0.05 per cent, the percentage of added nitrite that reacted in 5 hours varied between 1.2 at pH 1.6 and 5.8 at pH 3.4. No gas was evolved at pH 5.2 and above. It was concluded that it is unlikely that this reaction occurs to any marked extent in nature. This is because conditions for nitrite formation are not good at pH values that favor the reaction, and furthermore such low pH values are rather uncommon in soils and fresh waters. Any nitrites formed under such conditions are more likely to decompose to NO than to react with any amino acids or ammonia present.

Although the work mentioned seems to show that the nitrite-amino-acid reaction is of negligible importance in soils, it seemed desirable to learn more about the effect of pH and nitrite concentration on the initial rate and completeness of the reaction under especially favorable conditions. This requires that the experiments be conducted in an atmosphere of NO , instead of air, otherwise the nitrite decomposes quickly when added to an acid solution, as already emphasized (3). The present paper presents data obtained under such conditions at various pH values and concentrations of NaNO_2 .

EXPERIMENTAL PROCEDURE

The experiments were conducted in the standard type Van Slyke apparatus used for determination of amino acids. Certain modifications of the usual technique were necessary, however, since dilute solutions of NaNO_2 and 1 per cent phosphate buffer solutions were used. The NO was produced in an outside generator by adding a 30 per cent solution of NaNO_2 to glacial acetic acid. The

reaction chamber of the Van Slyke apparatus was filled with the buffer solution, and the burette with water, so that all air was driven out of the system. Pure NO was next introduced into the reaction chamber from the outside generator after first being bubbled through a NaOH trap for removal of any traces of acid spray. The apparatus was then ready for addition of the amino acid and the NaNO_2 . Varying concentrations of NaNO_2 were used, based on the theoretical quantity needed to react with the 3.12 mgm. alanine added in all experiments. These are designated as 1X (2.42 mgm. NaNO_2), 5X, 25X, and 126X. By means of the Ostwald pipette, 1 ml. of alanine solution was first added to the reaction chamber and then 1 ml. of NaNO_2 solution of the desired concentration. After the vessel

TABLE 1
Percentages of amino nitrogen converted into nitrogen gas at the 126X and 25X concentrations of NaNO_2

pH OF BUFFER	NITROGEN GAS EVOLVED IN			
	20 minutes	1 hour	1 day	3 days
	%	%	%	%
<i>126X concentration of NaNO_2</i>				
2.1	38.3	57.9	95.8	101.9
3.1	32.3	51.9	92.1	104.0
4.1	15.8	29.3	87.4	80.6
5.3	14.8	18.2	82.6	81.4
6.2	9.0	14.8	71.8	81.3
<i>25X concentration of NaNO_2</i>				
2.1	23.8	60.9	78.0	95.8
3.1	12.6	26.4	63.8	82.8
4.1	5.9	15.8	47.4	77.5
5.3	4.9	12.0	45.3	62.4
6.2	0.0	9.1	2.5	13.6

was shaken to assure thorough mixing, it was allowed to stand for the desired time. The NO was then absorbed in the usual manner by means of a KMnO_4 solution, and the residual nitrogen gas measured in the burette.

RESULTS

The extent of conversion of amino nitrogen into nitrogen gas at various pH values and with different concentrations of NaNO_2 during periods of 20 minutes to 3 days is shown in tables 1 and 2. No claim is made for extreme accuracy of the results, since the technique used is more difficult and less accurate than that used in the usual amino acid determination. The main source of error encountered was the evolution of traces of a gas other than nitrogen, presumably oxygen, from the KMnO_4 solution. This error, which was appreciable only for the longer reaction times, was corrected for by the use of suitable controls. The results

reported in tables 1 and 2 are the averages of two or more determinations for any given set of experimental conditions.

A detailed discussion of the results is unnecessary. At the highest concentration of NaNO_2 used, some nitrogen gas was produced by the nitrite-amino-acid reaction at all pH values from 2.1 to 6.2. The more acid the medium, the more rapidly the reaction proceeded. Likewise, the percentage of the amino nitrogen converted to nitrogen gas under all conditions increased with time of reaction. The amino nitrogen was completely converted to gas within 3 days or less only where the largest excess of NaNO_2 was added, and then only at a pH of 3.1 or lower.

At the lowest concentration of NaNO_2 used (table 2), which is higher than is commonly found in nature, no nitrogen gas was formed during a period of 1 hour at pH values above 4.1. Even at pH 2 to 3 only 9 per cent of the amino nitrogen was converted into gas during this period.

TABLE 2

Percentages of amino nitrogen converted into nitrogen gas at the 5X and 1X concentrations of NaNO_2

pH OF BUFFER	5X CONC. NaNO_2		1X CONC. NaNO_2	
	Nitrogen gas evolved in		Nitrogen gas evolved in	
	1 hour	3 days	1 hour	3 days
	%	%	%	%
2.1	22.9	94.4	8.9	35.6
3.1	14.8	78.9	8.9	20.2
4.1	11.9	53.8	7.0	6.1
5.3	10.8	17.1	0.0	5.9
6.2	7.0	10.8	0.0	0.0

The results reported here serve to extend our knowledge of the extent of the reaction at various pH values and concentrations of reactants under conditions made especially favorable. Failure to obtain the formation of nitrogen gas under these conditions would seem to establish that such a reaction is extremely unlikely to occur in air. Likewise, the formation of gas constitutes no proof that gas would be formed if air were substituted for the NO , since nitrite is much less stable in air. The present results serve as a supplement to those already reported (3). So far as comparable, they are in complete agreement with these earlier results and confirm the conclusion previously reached, namely, that loss of gaseous nitrogen as a result of the nitrite-amino-acid reaction is of minor importance in soils and plants.

SUMMARY

Laboratory studies dealing with the reaction of NaNO_2 with an amino acid to form nitrogen gas in solutions buffered at various pH values, and maintained in nitric oxide, are reported.

Nitrogen gas was formed to at least some extent over the pH range of 2.1 to 6.2. The initial rate and completeness of the reaction decreased with decrease in acidity and concentration of nitrite added. Only at the highest acidity (pH 2.1) and at the highest concentration of NaNO_2 (126 times theoretical) was the reaction complete within a 3-day period. At concentrations of nitrite corresponding most closely to those found in soils, no nitrogen gas was formed during a period of 1 hour at pH values above 4.1, and even at higher acidities only 9 per cent of the amino acid reacted. In air, nitrous acid decomposes so rapidly that there would be much less opportunity for the reaction to occur. Appreciable loss of gaseous nitrogen from soils by this mechanism, therefore, seems improbable.

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A NOTE ON THE PRESSURE PLATE-MEMBRANE APPARATUS

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Received for publication November 12, 1951

The advantages of the pressure plate-membrane apparatus over direct suction methods have been adequately described in the literature. Pressure plate and pressure membrane apparatus are similar in every respect but that of the composition of the permeable membrane. In each case, this is chosen to (a) allow water continuity and movement from the soil water in the sample in contact with the membrane to the free water outside the cell; (b) allow free salt diffusion through it; and (c) prevent rapid diffusion of the compressed gas out of the pressure cell. Pressure plates of sintered glass are generally restricted to pressures of less than 2 atmospheres, whereas membranes of cellophane or Visking sausage casing may be used for pressures up to 177 atmospheres (10). For convenience, the expression "pressure plate" is used in this paper, regardless of whether membrane or plate is involved.

Pressure plate apparatus has been used to obtain soil-moisture-hydrostatic-pressure relationships for many diverse experiments described in the literature (1, 2, 4, 5, 6, 8, 9, 13). In most of these experiments, the results have been applied in further investigations without comment on their accuracy, and very often the description of exact procedure has been omitted. L. A. Richards² has stressed that pressure cells can be operated in many ways that will give wrong results. The purpose of this note is to draw attention to the requirements for obtaining the true equilibrium moisture content under ideal experimental conditions and to distinguish this from the "equilibrium" moisture content determined when water flow from the cell has apparently ceased for any given applied pressure (where the time taken for samples 1 cm. thick generally varies between 6 and 48 hours, depending on the texture of the soil). This "equilibrium" moisture condition is difficult to pinpoint, as the flow of water will approach zero asymptotically with time. It is suggested that this so-called "equilibrium" be called the "time equilibrium," as it will vary with the time of sampling.

In experiments on samples of separated clays in this laboratory, it was noticed that samples did not reach an equilibrium moisture content for any given air pressure applied to the sample when water flow had apparently ceased from the cell but that with time the samples became progressively drier.

The experimental conditions under which behavior occurred were as follows: a membrane of cellophane; atmospheric air, compressed and driven straight into the cell at the relative humidity conditions then prevalent in the laboratory air,

¹ The author acknowledges the helpful comments and criticism concerning soil-moisture equilibria by E. C. Childs of the A. R. C. Soil Physics Unit, Cambridge, England, and by L. A. Richards of the U. S. Salinity Laboratory, California.

² Private communication.

that is, the air in contact with the clay contained water vapor of unknown and uncontrolled pressure.

In this experiment the cellophane membrane was replaced as often as the leak of air through it made it impracticable to keep the pressure up in the cell. (The membrane was replaced when the pressure had fallen to zero in 24 hours after the cell was charged.) Punctures and leaks in the cellophane appear erratically and very quickly, and the total loss of air during the course of the experiment cannot in any way be compared to this maximum leakage rate of 5×10^{-5} cc./sq. cm./second/atmosphere. The sample of clay lay in good contact with the membrane and had a maximum thickness of 7.5 mm., which, from the literature, would be assumed to have reached "time equilibrium" in 2 days.

The continuous loss of water from the sample was presumed to be caused by the lower water vapor pressure of the air supplied to the cell in contrast with

TABLE 1
*Decrease in moisture content with time for continuous supply of "dry" air to Na-saturated Putnam clay**

PRESSURE OF GAS APPLIED	TIME OF MAINTENANCE OF GAS PRESSURE	MOISTURE CONTENT OF SAMPLE AT END OF PERIOD†
<i>lb./sq. in.</i>	<i>days</i>	<i>per cent‡</i>
60	0	129.5
60	26	111.5
60	41	77.9
60	29	69.1
120	45	60.5
120	67	38.8

* Originally suspended in $\frac{1}{2}$ N NaOH solution.

† Duplicate samples were taken in some cases: the samples were not returned to the cell after sampling.

‡ Of dry weight.

that which would be in equilibrium with the clay if there were no movement of air. No loss of moisture due to the actual changing of membranes is likely, as the cellophane was water-saturated before use. The loss of water due to exposure of the samples to the laboratory atmosphere during sampling and changing of membranes can be ignored because the total exposure time was small and the air to which the samples were exposed was of the same relative humidity as the air supplied to the cell. The error due to these causes in each stage in table 1 is expected to be less than 2 per cent. The results in table 1 demonstrate that long after water flow from the pressure plate apparatus had ceased, that is, after "time equilibrium" was reached, the clay continued to lose moisture by gaseous diffusion, and under the stated conditions it becomes impossible to define the moisture content for a given applied pressure, which was the original object of the experiment.

In some pressure plate experiments described in the literature (7), pure nitrogen gas has been used and the apparatus designed to allow fairly extensive mem-

brane diffusion without fall in pressure. Seemingly, under these conditions the gas supplied will be water vapor free. As long as gas escapes there will be a continuous loss of water from the samples, in an attempt to bring the gas in the cell to a relative humidity in equilibrium with an ever-decreasing moisture content of the sample.

From these premises, it would seem to be necessary to premoisten the air or gas supplied to the pressure plate to the relative humidity with which the sample will be in equilibrium at the pressure applied.

In the following section the theoretical considerations necessary to calculate the relative humidity to be encountered inside the pressure plate apparatus are outlined.

THERMODYNAMIC CONSIDERATIONS

By thermodynamic reasoning it can be shown that the relation between the osmotic pressure of a solution at zero hydrostatic pressure and the vapor pressure in equilibrium above it is given by

$$\pi = RT/V \ln p_0/p \quad (1)$$

where R is the gas constant, T the absolute temperature, p the vapor pressure of the solution and p_0 the saturation vapor pressure at the same temperature, and V the partial molar volume of water. If the partial molar volume is assumed to be almost the same as the molar volume of pure water, expression (1) becomes at 20°C. and in centimeters of water

$$\pi = 3.18 \times 10^6 \log_{10} (p_0/p) \quad (2)$$

Similarly it can be shown that an identical relationship exists between the pressure applied to the soil in the pressure plate apparatus, or between the suction (pressure deficiency) in a Haines type apparatus, and the lowering of water vapor pressure in equilibrium with a soil which has zero osmotic pressure; namely, at 20°C. and when the applied pressure is measured in centimeters of water

$$H = 3.18 \times 10^6 \log_{10} (p_0/p) \quad (3)$$

In a soil containing ions, and hence with some osmotic pressure, and also in the pressure plate apparatus under a pressure H , the vapor pressure lowering relation becomes at 20°C.

$$\pi + H = 3.18 \times 10^6 \log_{10} (p_0/p) \quad (4)$$

H , the pressure to be applied to the soil, is easily measured. The osmotic pressure when water has stopped leaving the sample and the sample has reached equilibrium under the applied conditions cannot be determined, however, until the experiment is finished; but as the order of π is required before the experiment can begin, an approximation must be made. This is done by subjecting the sample to the required H without any vapor pressure considerations, and as quickly as possible and with a minimum of gas leakage collecting a specimen of the exudate.

The osmotic pressure of this exudate, though probably less than that at equilibrium with the applied H and π , can be substituted in (4) to provide the order of magnitude of the water vapor pressure required for the air or gas used in the cell.³

APPROXIMATE CALCULATIONS OF VAPOR PRESSURE

For dilute undissociated solutions

$$\pi = cRT \quad (5)$$

where c is the concentration of the solute in moles.

For solutions of salts

$$\pi = \Sigma a_i RT \quad (6)$$

where a_i is the activity of each ion species in gram-ions, and where $a_i = \gamma_i c_i$, and γ_i is the activity coefficient of each species. A discussion of the activity

TABLE 2

Osmotic pressure for solutions of uni-univalent electrolytes assumed to be completely dissociated, and equivalent total pressure applied to samples in pressure plate apparatus in terms of actual applied gas pressure and osmotic pressure

NORMALITY OF SOLUTION ($c_i = a_i$)	OSMOTIC PRESSURE* π	EQUIVALENT TOTAL PRESSURE* ($\pi + H$) UNDER APPLIED GAS PRESSURES,* H , OF			
		100	1,000	10,000	100,000
0.01 N	497	597	1,497	10,497	100,497
0.1 N	4,972	5,072	5,972	14,972	104,972
1 N	49,720	49,820	50,720	59,720	149,720

* All pressures in centimeters of water at 20°C.

coefficient, γ_i , and its variation with μ , the mean ionic activity, is out of place here. It suffices to say that the value of γ_i for commonly occurring salt concentrations is tabulated in text books dealing with electrolytic solutions in any detail, for example, Harned and Owen (3).

It is necessary, however, to give the order of the osmotic pressure effect on vapor pressure. As a first approximation it will suffice to take γ_i equal to unity, that is, $a_i = c_i$, when equation (6) at 20°C. and in centimeters of water becomes

$$\pi = \Sigma c_i \times 2.486 \times 10^4 \quad (7)$$

Table 2 gives the value of π and of the corresponding sum of $\pi + H$ for uni-univalent electrolytes. The conversion of these total pressures in centimeters of water to relative humidity (p/p_0) by (4) is given in table 3.

From these calculations, it would appear that rarely will the relative humidity in the pressure plate apparatus be theoretically less than 90 per cent, and as a first approximation it would also appear that use of pure water as a presaturator would give vapor pressures much nearer to those required by theory than those resulting from use of dry air or gas.

³ At equilibrium, the true value of $H + \pi$ is precisely determined by the freezing point depression of the sample (12), when $\log_{10} (H + \pi) = pF$.

To obtain the concentration of the ion species in the soil solution, c_i , it is necessary to examine the first exudate from the pressure plate apparatus at the applied pressure, H , by, for example, electrical conductivity measurements or quantitative analysis, and then convert this c_i to a_i ($= \gamma_i c_i$) by use of appropriate tables of activity coefficients (3); or to obtain a_i , which is theoretically required for equation (7), the exudate must be examined by either freezing point depression measurements (which, being a colligative property, would be the most satisfactory method leading to a calculation of vapor pressure lowering) or by e.m.f. measurements where suitable electrode arrangements are possible.

As the experiment progresses, each subsequent exudate would be examined and a_i or c_i determined, the vapor pressure corresponding to these activities could be calculated, and a suitable presaturator of the appropriate relative humidity used.

TABLE 3

Relation of applied gas pressure and strength of soil solution in terms of uni-univalent electrolyte to relative humidity of gas in equilibrium with the soil

NORMALITY	APPLIED PRESSURE			
	100	1,000	10,000	100,000
0.01 N	.9995	.9989	.9924	.9298
0.1 N	.9963	.9957	.9892	.9268
1 N	.9646	.9640	.9576	.8972

The most suitable presaturators, requiring little attention, would allow repeated bubbling of gas through saturated solutions of salts in the presence of the solid phase. For example, a saturated solution of $K_2Cr_2O_7$ has a relative humidity of 98.4 per cent; K_2SO_4 = 97.3 per cent; Na_2HPO_4 = 95 per cent; K_2HPO_4 = 92 per cent.

DISCUSSION

When the diffusion of gas through the membrane of the pressure plate apparatus is appreciable, the presaturation of the gas or air to a given water vapor pressure (to be in equilibrium with both the pressure of gas applied and the osmotic pressure of the soil solution and calculated as previously outlined) is necessary for the soil to reach equilibrium. The greater the pressure or the salt content of the sample, or both, the lower the equilibrium relative humidity should be. The use of a drier gas will cause the sample to become progressively drier as the gas continues to leak through the membrane of the cell. With the use of a gas wetter than that required, no true equilibrium can be reached, as the sample will attempt to expand and adsorb water to reach equilibrium with this high relative humidity while exuding water under the effect of the applied pressure. With the correct relative humidity of applied air pressure, the wet sample will dry until as much water will leave the cell, in the form of vapor, as enters, and the sample will be at the theoretically required or hydraulic equilibrium moisture content. The "time equilibrium" condition, reached by the

present practice of sampling when liquid water flow from the sample stops, is likely to be wetter than the hydraulic equilibrium condition. At the moment, the only convenient method of determining when hydraulic equilibrium has been reached is by repeated sampling and weighing until constant moisture content is obtained.

The use of membranes, such as Visking sausage casing, has in fact reduced diffusion losses of gases considerably, and the error described in the preceding paragraph will be small when the starting point is either a dry or a wet gas, provided sufficient time is allowed for thermodynamic equilibrium to be reached. In the ideal experiment where there is no loss of gas through the membrane, the sample will be in true hydrostatic equilibrium with the applied pressure as soon as water flow finishes, since there is only a limited volume of air to reach equilibrium relative humidity. The moisture content at hydrostatic equilibrium will, of course, be equal to that obtained by hydraulic equilibrium methods.

In cells where loss by diffusion is so small that a sample is able to lose water through the membrane to satisfy the applied pressure and simultaneously moisten the constant amount of enclosed gas to the equilibrium vapor pressure without itself being overdried, it is obviously improper to have more than one sample enclosed in the cell. In this case each soil, having its own osmotic pressure, will have a different equilibrium water vapor pressure, which could not be satisfied for all soils in one cell. Richards (10, 11) and Richards and Weaver (8, 9) have described cells specifically designed to accomodate large numbers of different soil samples simultaneously. Related to this error, and developing from the use of air compressors and automatic pressure controls to maintain constant pressure, is the linking of several cells to a common pressure line, thereby allowing water vapor diffusion between the various soils in the various cells. It is expected that this error will be negligible. In multisoil cells though no evidence is yet available, the error will obviously be much greater. Though both "time equilibrium" and hydraulic equilibrium for a particular rate of air flow and relative humidity may be attained, the experiment will not allow true thermodynamic equilibrium for each sample. In this case, hydraulic equilibrium will differ from thermodynamic equilibrium, and even hydraulic equilibrium will vary with experimental procedure, but not with time.

Although operators have obtained consistent and replicated results with a nonideal experimental procedure, it is likely that if the time to attain equilibrium or the number of samples in "equilibrium" with one another were changed, different moisture contents for each pressure would be obtained. Each operator, however, will have to decide whether the information required justifies the additional trouble and expense of finding how great is the difference between "time equilibria" and hydraulic equilibria. It is suggested that future published results from pressure plate apparatus should state precisely how they have been obtained.

L. A. Richards has drawn to the author's attention the question of temperature control. Equations (1) and (4) are both dependnet on temperature, and the equivalent relative humidity should be calculated for the prevailing laboratory

temperature. Variations in temperature during an experiment at a given pressure alter the relative humidity and may even produce dew. In this case, even "time equilibrium" as commonly determined will vary and hydraulic equilibrium cannot be attained.

SUMMARY

Results are given to show that the moisture content of a soil in a pressure plate apparatus decreases indefinitely when a dry gas is used and gaseous diffusion through the membrane is continuous.

It is pointed out that for any soil sample there is only one water vapor pressure of the applied gas which can be in thermodynamic equilibrium with the sample. This vapor pressure depends on the osmotic pressure of the soil solution and the pressure of the gas applied.

From the literature, it would appear that generally the moisture content of the sample is determined for a given pressure when the outflow of liquid water through the membrane has become negligible. It is suggested that this condition be called a "time equilibrium," which will vary with the time of pressure application. It is further suggested that the condition under which the humidity of the gas leaving the apparatus is the same as that entering be called "hydraulic equilibrium." Except for multisoil apparatus, this equilibrium will be thermodynamically true and the relative humidity involved will be the one in equilibrium with both applied pressure and osmotic pressure. True hydrostatic equilibrium can be reached only with an ideal membrane that is permeable to water but completely impermeable to gases.

Under the conditions of hydraulic equilibrium and ideally of hydrostatic equilibrium, it is possible to relate a given moisture content to a given applied pressure with no ambiguity.

The requirements for hydraulic equilibrium are outlined and examples of deviations from these requirements are given.

It is pointed out that the difference between "time" and "hydraulic" equilibria has not yet been investigated, but depending on the subsequent use made of the results, the difference may not justify changes in existing procedures. It is suggested that precise experimental conditions be included when results for pressure plate-membrane apparatus are reported.

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LESSONS FROM THE FIRST HALF CENTURY OF SOIL SURVEY: II. MAPPING OF SOILS

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Received for publication September 7, 1951

The first paper in this series (7) presented a brief sketch of the development of soil classification in the United States since soil surveys were begun in 1899. It also outlined a number of the lessons evident from that development. Similarly, a review of the field methods used over the half century is instructive because the changes in approach have been as great as the changes in classification. A number of lessons, especially useful in formulating mapping programs, can be taken from experience in the United States.

EARLY SOIL MAPPING

In the first "detailed" soil surveys, the field men covered large areas during each season. For example, according to the first report of field operations (11), 80 man-days were required to map 400 square miles in the Connecticut Valley of Massachusetts and Connecticut in 1899. This is an area of brown podzolic and related soils. Five years later, Tama County, Iowa, was mapped for a total cost of \$1,000 (2). Tama County, with an area of 710 square miles, lies in the heart of the prairie soil region.

The early soil maps have simple patterns with large individual areas. For example, the soil map of the Connecticut Valley shows 10 soils in the 400 square miles, whereas that for Tama County shows five soils in 710 square miles. These patterns are a reflection of what was known about soils and their classification in the first decade of the American soil survey. Early instructions to field parties (9, 11) state that areas of distinct soils should be separated on the field sheets whenever they were $\frac{1}{4}$ mile or more in diameter. As time passed, the size of the smallest area to be shown on the map was gradually reduced from 40 to 10 acres. Instructions in 1914 (10) state that an area of 10 acres is the smallest that can be conveniently shown on a published map with a scale of 1 inch equals 1 mile (1:63,360).

The early reports of field operations gave some emphasis to the adaptation of soils to a crop or crops. Fifteen years after the first survey had been made, the instructions (10) carried the following statement: "The purpose of a soil survey is to map, classify and correlate soils, to determine and describe their field characteristics, to report on the actual use being made of the soils and on their adaptation to various crops, so far as can be determined, and upon the relative productiveness of the several soil types." From a study of the maps and text, however, it is clear that the field scientists were thinking in terms of broad areas with important acreages of soils suitable for a crop or crops. They were not thinking of the specific use and management of soils within fields and of predicting yields from those soils.

Even during the first years of soil survey, distinctions were made in the nature of the field work from one place to another. The first report (11) shows that field men in 1899 mapped 5 square miles a day in the Connecticut Valley of New England and 1 square mile a day in the Pecos Valley of New Mexico. The former region was one of general farms in which small bodies of soil were not thought to be important. The latter was an irrigated area in which smaller soil areas were obviously important to success or failure of a farmer. Some time within the first decade of the soil survey, distinctions between detailed and reconnaissance surveys were made on the basis of the network of field observations.

COMPARISON OF PRESENT AND EARLY MAPPING

The examination of the land is far more detailed and thorough at present than it was in the soil surveys of the first decade. The modern soil survey is the most detailed examination of land being made over extensive areas. The differences between early and modern field methods are evident in rates of progress, in the number of soil units recognized in field work, and in the scale and complexity of published soil maps.

In making a modern basic soil survey, the field men must see every one of the boundaries throughout its entire course. This need, plus the additional studies made in present-day surveys, is responsible for the sharp increase in time spent per unit area. Putting it another way, this more thorough examination of the land surface is a primary reason for the much lower rate of progress per man-day of field work.

In the soil survey of Tama County, Iowa, in 1904 (2), the field man covered 5 square miles a day. Field work in the same county 30 years later was at an average rate of 1 square mile per man-day. At present, a competent field scientist can cover 200 to 640 acres a day, depending on the complexity of the soil pattern and the relationships between distribution of soils and readily observable features such as topography. Many more observations per unit area are made now than were made in the early soil surveys, and many more areas are delineated on the soil maps.

The classification is much more detailed now than it was 40 years ago: where five soil types were mapped in Tama County in 1904 (2), 50 soil types and phases were recognized in 1938 (1). Similar comparisons may be drawn from other areas. Only 14 soils are shown on the map of Grainger County, Tennessee, made in 1906 (5), whereas 128 soil types and phases are shown on the map issued in 1948 (3).

The increase in time per unit area for field work would be even greater in the United States were it not for the aerial photographs that are available generally for use as base maps. Only 20 years ago, soil scientists spent part of their time in the field making traverses to provide ground control for the construction of base maps. At that time, base maps on which soil boundaries could be plotted were not generally accurate enough to warrant the detail now common in our basic soil surveys. If the soil map of a given area is to be highly detailed, soil boundaries must be placed accurately with reference to local features, such as

streams, houses, and roads. This can be done rather easily on aerial photographs. The quality of a detailed soil survey anywhere depends greatly upon the quality of base map materials available. With aerial photographs generally available in the United States, the soil scientist can give his time to the study of soils and the sketching of soil boundaries. Without those photographs his problem of keeping himself located on the ground so that his boundaries could be placed with the same accuracy would be immeasurably greater (6).

Comparisons of early and present-day soil maps for the same area clearly demonstrate the change over the first half century. Detailed soil maps were published at a scale of 1 inch equals 1 mile (1:63,360) in the early days of the soil survey and down to fairly recent times. Present detailed maps are published largely at scales ranging from 2.6 inches equals 1 mile (1:24,000) to 2 inches equals 1 mile (1:31,680), with a few at a slightly smaller scale (1:48,000). Thus the map for a given area is now three to eight times as large as was the map in 1899. Furthermore, the modern map carries about 16 times as many miles of soil boundaries. This is at once apparent from a comparison of the two maps of Grainger County, Tennessee, one published at a scale of 1:63,360 in 1906 the other at a scale of 1:24,000 in 1948.

NATURE OF MODERN SOIL SURVEYS

The present concept of the soil survey is more inclusive and more explicit than that of 40 years ago. There are, however, many similarities in concept, as might be expected in a program that has developed continuously over the years. One function of the soil survey is to increase agricultural efficiency. Modern soil surveys are designed (a) to determine the characteristics of soils; (b) to classify them into defined units; (c) to establish and plot their boundaries on maps; and (d) to predict their suitability for various crops, grasses, and trees, their behavior under different use and management practices, and the yields of adapted plants under specified management systems (8). This concept is broader and more sharply defined than that expressed in statements prepared some 40 years ago (10). One of the main purposes of the soil survey, like that of other research, is to make predictions. To make sound predictions, however, it is necessary to accumulate a considerable body of knowledge about soils and their behavior.

Not all elements of the modern soil survey are considered in this discussion, although they are important in making adequate soil maps and sound interpretations. Furthermore, no effort is made to distinguish between the various types of surveys necessary in different landscapes and for different purposes. Readers who want more information about the nature and functions of soil surveys are referred to the soil survey manual (8).

The field mapping and associated research answer the first three purposes of the soil survey. From these studies come the determinations of important characteristics of soils, the classification of soils into types and phases, and the map showing their distribution and extent. The field mapping includes the work of walking across the land at intervals to examine and identify the soils and to

plot their boundaries on maps (usually aerial photographs). Prior to and concurrently with the field work of mapping, it is also necessary to make field studies of soil morphology and conduct various laboratory investigations. These are to determine the important characteristics for the classification of the soils and to improve the understanding of soil genesis. These studies provide information on such characteristics of soils as chemical composition, physical constitution, mineralogical nature, and cation-exchange relations. All this research, only part of which is effective in the production of soil maps, is necessary to proper definition and mapping and also adds to the general knowledge of soils. The information and knowledge thus gained provide the guide lines for the field scientists who make the maps and prepare interpretations. The validity of the classification, the quality of the maps, and the usefulness of the interpretations are direct reflections of the knowledge of the men doing the work, including the supervisors as well as the field scientists.

To answer the fourth purpose of the soil survey, the behavior of soils under different methods of handling must be determined. Predicting the yields of crops, grasses, or trees or the long-time effects of management practices on the soil cannot be accomplished from knowledge of the nature, extent, and distribution of soils alone. It requires the synthesis of data from several fields of knowledge, including the various branches of soil science. Judgments as to the usefulness of a soil for cultivation or for grazing can be made only with some form of agriculture in mind. The probable value of a soil for each of the alternative uses also depends upon the comparative prices of the expected products. Soil surveys provide data directly on the kinds, distribution, and extent of soils; additional sources of information must be drawn upon to determine the behavior of soils in agriculture, forestry, or engineering.

PROGRAM OF SOIL SURVEYS AND MAPPING

From experience with soil surveys over a half century in the United States, it follows that the chief purpose of a soil mapping program is to determine the nature, distribution, and extent of different soils. Mapping is also important, but less so, in testing and further developing the classification scheme.

To be useful for practical objectives, maps must show geographical areas that are homogeneous enough to permit the making of predictions about soil behavior for the purpose at hand. Small areas must be outlined where a high degree of homogeneity is necessary, as, for example, when farm advisors make specific recommendations for fertilizer use and crop rotations for specific fields. Broad areas with much lower degrees of uniformity can be used for blocking out lands that might be suitable for settlement in undeveloped regions. Consequently, information about the nature, distribution, and extent of soils is needed at a number of levels of generalization. The job in a program of soil mapping is to meet the various needs as quickly and completely as is feasible. Five successive steps are therefore suggested in this section for a program of soil mapping in undeveloped areas (4) where little is now known about the soils. The whole sequence of steps may not apply to every area, but some of the steps commonly

will. Which of the steps may be applicable will depend upon the progress already achieved.

1. First, a soil association map can be compiled from existing sources of information such as climatic data, topographic and geologic maps and reports, vegetation maps and reports, aerial photographs, notes by scientific travelers, and observations on reconnaissance trips. This map would be a first approximation, probably on a small scale, to show soil associations. The number of soil associations outlined on the map and the degree of homogeneity of each will be governed by the amount of information at hand. In some cases, the scale of the map upon which association areas are outlined becomes the limiting factor in the detail that can be shown.

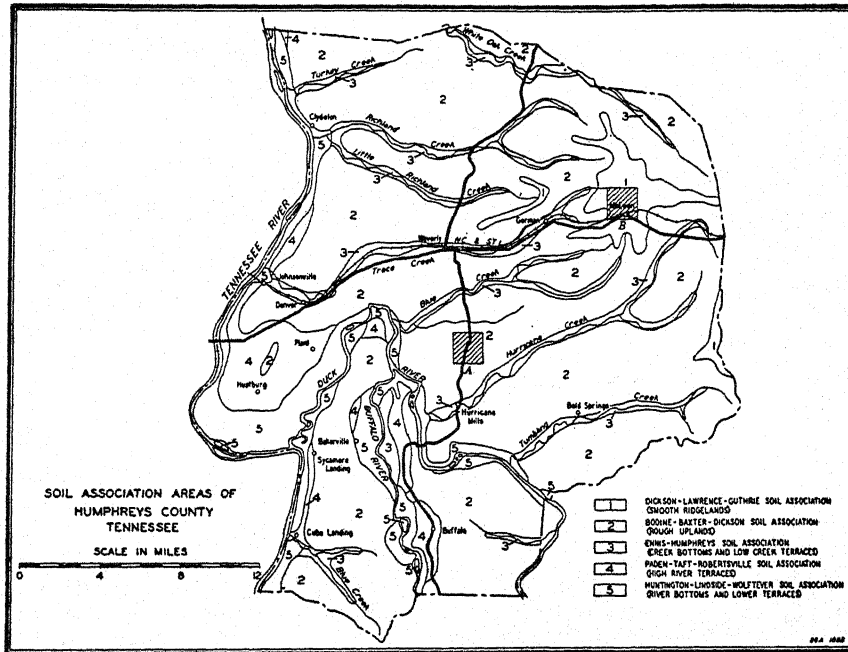


FIG. 1. MAP SHOWING SOIL ASSOCIATION AREAS IN HUMPHREYS COUNTY, TENNESSEE

The small cross-hatched blocks, A and B, are sample areas for which detailed soil maps are given in figure 2.

The several possible sources of information are not all of equal value. Information on climate, topography, geology, and vegetation—especially in the form of reliable maps—will be very helpful in plotting the boundaries of soil associations. Aerial photographs will also be extremely useful. Notes made by scientific travelers, other than soil scientists, will have limited usefulness but can be used to some degree in the absence of better information. By and large, reconnaissance trips by competent soil scientists will be especially helpful in obtaining reliable information. Such reconnaissance trips should be made wherever they are possible, either during original compilation of the map or to check it in the early stages of preparation.

Soil associations are areas or bodies of land with a characteristic and recurring pattern of soils. Thus, each association is uniform with respect to soil pattern rather than with respect to soil itself. For the most part, soils occur as small intermingled areas of soil types

and phases, usually unlike one another to some degree. In many ways, soil associations are like plant associations. Under natural conditions, certain plants grow together in an area. In the same way, certain soils characteristically occur together, and the area in which they occur in a characteristic pattern is a soil association. Both soil and plant associations are thus geographic units useful in providing a picture of a region.

To illustrate the concept further, a map of soil associations in Humphreys County, Tennessee (12), is shown in figure 1. Five associations are outlined in a county with a total area of 555 square miles, and the units shown have a high degree of uniformity of pattern. The principle of similarity of pattern from place to place within units will apply, however, whether the associations are narrowly or broadly defined. In the map shown in figure 1, the kinds of soils, the patterns they form, or both, differ from one soil association to the

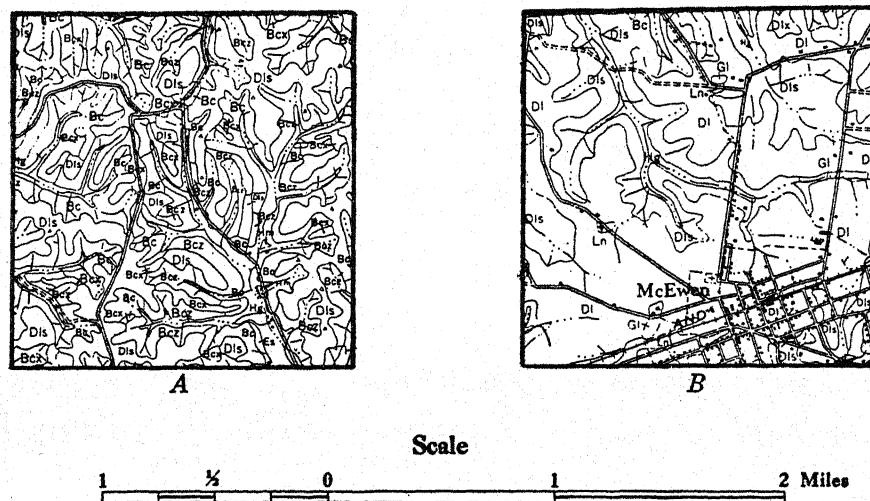


FIG. 2. DETAILED SOIL MAPS OF SMALL BLOCKS IN TWO SOIL ASSOCIATIONS IN HUMPHREYS COUNTY, TENNESSEE

Block A shows the soil pattern in the Bodine-Baxter-Dickson association; block B represents the Dickson-Lawrence-Guthrie association. Principal soil types and phases in the two blocks are: Bc, Bodine cherty silt loam; Bcs, Bodine cherty silt loam, slope phase; Bcz, Bodine cherty silt loam, steep phase; Dl, Dickson silt loam; Dls, Dickson silt loam, shallow phase; Ln, Lawrence silt loam.

next. The difference is indicated in figure 2 (A and B), which consists of detailed soil maps of blocks in two of the soil associations shown in figure 1. The much more intricate soil pattern of the Bodine-Baxter-Dickson association (A) is immediately evident. Differences in the proportions of Dickson soils, common to the pattern in both associations, are also readily evident. Additional patterns of soils in an association are indicated by the block diagram showing geographic relationships in north-central Iowa, included in the earlier paper of this series (7).

2. Detailed soil surveys should next be made of carefully selected sample areas of the major associations outlined in the first step. Each of these might cover 1 to 30 square miles, the size and number depending upon the soil pattern in the area. During the course of these detailed surveys, the classification of the soils into types and phases should be developed. Concurrently with the mapping of the sample areas, investigations should be carried on so far as feasible to determine the properties of soils and their behavior in agriculture, forestry, and engineering.

3. As the soil surveys of sample areas are completed, keys to show relationships among soils and groupings of various kinds should be prepared. For any given area, simple keys should be constructed to facilitate identification by agricultural advisors and others of the soil types or phases mapped in the sample area survey. These keys need only point out local relationships; they need not show relationships of soils in the area to those of larger regions. Examples of useful keys to aid in local identification of soils are charts showing relationships of the individual types and phases to parent materials and drainage. Soils can be grouped to illustrate genetic relationships and to aid users of soil survey data, especially in agriculture and forestry. A number of different kinds of groupings are possible, depending upon the purpose at hand. For example, soils can be grouped into series, families, and great soil groups to show genetic relationships. They may be grouped according to their suitability for a crop or a combination of crops. They may be grouped according to use-capability within a specified agriculture. These latter steps must go beyond the limits of soil science alone and draw upon fields such as agronomy, horticulture, and forestry. Thus, this becomes an interpretative step, based in part upon the soil survey and in part on other sources.

4. After the sample areas have been mapped, the second approximation of the soil association map can be prepared. The boundaries as first outlined can be refined in many instances and the associations themselves can be defined much more completely. Data from sample areas will permit far more specific descriptions as to patterns and percentages of soil types and phases within each association.

The second approximation of the soil association map can be used as part of the basis for public planning in the use of land. It will be helpful in such planning as is required in rural zoning, for the guidance of land settlement, and in any search for possible sites for irrigation and drainage projects.

5. After the revised soil association map is available, the soil surveys should be extended over the whole region as rapidly as the knowledge of the soils and the available funds will permit. It will probably be true without exception that available funds will not permit the mapping of soils of an entire country or district within a short time. Moreover, it will certainly be true without exception that the adequacy of surveys depends at all times upon the results of other types of research, research that may not be completed for a number of years. The first detailed soil surveys are commonly more useful in pointing out major research problems than in solving those problems. They will have important usefulness in a land improvement program, to be sure, but they will also be found inadequate for a number of purposes in the future as a program of soil research goes forward. Consequently, it would not be desirable to outline a program for the complete mapping of a country within a few years even though funds might be obtainable.

Areas to be mapped should be selected on the basis of need and interest. As these surveys are made, it is of extreme importance that investigations to determine the characteristics and behavior of the soils accompany the mapping program. Research on the properties and responses of soils to management should go forward at the same time as do the programs of soil classification and mapping.

This approach has a number of advantages for regions where limited information on the nature and distribution of soils is at hand. First, the existing information about soils is assembled, organized, and analyzed so as to be of maximum usefulness. This information is not only helpful in dealing with broad questions covering large regions but it also provides a much better basis for the selection of areas in which detailed surveys will be made. The latter can go forward as rapidly as resources will permit in the sample areas. The combined use of a soil association map with basic soil surveys of sample areas permits the making of detailed predictions by soil types and phases as well as more accurate defini-

tions of the soil associations themselves. Much information already at hand can thus be placed in a form usable by agricultural advisors, government officials, and others. It is of the utmost importance in following this approach to make information, including maps, keys, yield predictions, and the like, available to agricultural advisors who must deal with individual farmers. These aids will help the advisors to become better acquainted with the soils in their respective areas and will become a part of their working knowledge.

At the other extreme, the approach will provide data of great usefulness in regional programs of development. The best possible synthesis and appraisal of available knowledge about the soils of a region are essential in the intelligent planning of programs for settlement, for irrigation, for the building of roads and railways, and for many other purposes. Settlement experience in the western United States demonstrates beyond question the possible usefulness of prior knowledge of soil resources. Most of the area was occupied without such knowledge and with great waste of effort and wealth. Abandoned homesteads over much of the Great Plains have served as graphic evidence of settlement attempts without adequate understanding of soil potentialities. Full use of the information available about the natural resources of the Great Plains prior to settlement could have forestalled many of the failures. Full use of the knowledge available or obtainable about soils and their behavior is even more important in regional development today than it was 50 years ago. Tested methods for assembling and evaluating information about soils are important parts of the lessons that can be learned from the first half century of soil survey in the United States.

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BOOKS

Air Pollution. LOUIS C. McCABE, Chairman. McGraw-Hill Book Company, Inc., New York, 1952. Pp. 847. Price \$12.50.

This book contains the proceedings of the United States Technical Conference on Air Pollution, sponsored by the Interdepartmental Committee on Air Pollution. It is made up of 97 papers by specialists in agriculture, analytical methods, equipment, health, instrumentation, legislation, and meteorology, as related to this problem. The general sessions that followed the presentation of these papers were held May 3-5, at the Wardman Park Hotel, Washington, D. C. Much of the discussion had to do with effects of fluorine on soils, plants, and animals. Sulfur compounds, weed-killing chemicals, smokes, dusts, and fogs were reported on in relation to the health and well-being of plants and animals, including man. By the very nature of the problem, a wide variety of technical skill and knowledge was brought to bear on the subject. The book is a very important and highly useful compendium of information on air pollution. It will be of great interest to many persons.

American Potato Yearbook. Edited by JOHN C. CAMPBELL. C. S. Macfarland, Jr., Westfield, N. J., 1952. Pp. 80. Price, paper-bound, \$2.

The purpose of this publication is to record the associations engaged in the improvement of the potato industry, potato periodicals, acreages, yields, selling prices, seedstocks, certification, scab control, and storage requirements. One of the most interesting features is the long list of research projects on Irish potatoes and the names and addresses of those who are in charge of the work being done. This is a very useful reference book.

Annual Review of Plant Physiology. Volume 3. Edited by DANIEL I. ARNON AND LEONARD MACHLIS. Annual Reviews, Inc., Stanford, Calif., 1952. Pp. 369. Price \$6 plus shipping charges.

The 15 papers in this volume deal with micronutrient metals, glycolytic enzymes, phosphorylated compounds, auxins, growth regulators, transport of organic compounds, leaf proteins, low temperature preservation, virus diseases, ion absorption, assessing nutritional requirements, photosynthesis, physiology of flowering, carboxylating enzymes, and tree physiology. Each paper is well documented, references being given to the work of some 1,500 research workers. On the whole, the material is well presented. This series of reviews should be at hand for ready reference by all those who are concerned with soil-plant research.

Biochemical Preparations. Volume 2. Edited by ERIC G. BALL. John Wiley and Sons, Inc., New York, 1952. Pp. 109. Price \$3.

The editor-in-chief of this volume was Robert C. Sealock, who assembled the methods and checked most of them in his laboratory previous to his death in August, 1951. The preparations include cytochrome, globulin, oxycasein, phos-

vitin, lactate dehydrogenase, sodium pyruvate, phosphoryl-enolpyruvic acid, glycerophosphoric acid, glucose phosphate, C14 labeled sucrose, fructose diphosphate, inosose, inositol monophosphate, glutamic acid monohydrate, aspartic acid, benzyl cysteinylglycine, methyl carbobenzoxyglutamate, glutathione, diphosphopyridine nucleotide, phosphorylcholine, oleic acid, and methyl ricinoleate. This is a very valuable book for those who are concerned with the preparation of these and related compounds.

The Biotic World and Man. By LORUS J. MILNE AND MARGERY J. MILNE. Prentice-Hall, Inc., New York, 1952. Pp. 588. Price \$9.

"An education is what remains as an individual's point of view and mode of thinking after most of the details learned in school have been forgotten. Many of the facts may seem useless in prospect and in immediate retrospect. So are the weary steps by which a person climbs a mountain. But without the steps there is no view." The authors have provided the steps by which the mountain can be climbed but they have also made it so interesting and attractive along the way that the weariness has been eliminated. The approach to the subject is well illustrated by a diagram that shows the steps of observation, hypothesis, prediction, and planned experiments that lead to continually higher levels of factual information. The development of the subject gets under way when spontaneous generation is considered. The authors then proceed by many excellent illustrations and by highly lucid discussions to deal with variety, forms, development, abundance, haunts, history, and value of life and with a final look toward the future. This is a truly remarkable book, which is destined for wide distribution and a very high degree of usefulness in understanding man and the life that surrounds him.

The Conservation Yearbook. Edited by ERLE KAUFFMAN. Monumental Printing Company, Baltimore, 1952. Pp. 288. Price, paper-bound, \$5.

The editor of this yearbook has assembled "a directory and guide to facts, figures, and people in American conservation." The general headings include conservation legislation, organizations, the conservation estate, facts and figures, and publications. Almost any type of information one may require on conservation and closely related subjects can be found in this publication, the assembling of the material for which must have required a great deal of careful work on the part of the editor and those associated with him in this enterprise. A highly useful index is appended.

De Bodemkartering van Nederland, Deel X. J. Schelling, Wageningen, Netherlands, 1951. Pp. 139, maps 10, profiles 4.

The summary of the soil survey of northern Limburg, with which this report deals, is repeated in English. One of the most significant statements in the summary is: "As the need for mineral plant food can be met by applying fertilizers, the water supply is in many cases the decisive factor. The distinctions on the map are strongly related to the water supply on the different soil types."

Hydroponics, the Bengal System. By J. SHOLTO DOUGLAS. Oxford University Press, London, 1951. Pp. 147, plates 16. Price \$2.

The author of this little book is working in West Bengal, where he has applied the techniques of hydroponics and offers some suggestions with regard to their improvement in practice. The several chapters deal with plant growth, apparatus, nutrient mixtures, practical applications, general techniques, commercial possibilities, deficiencies, miscellaneous matters, and an estimate of the future possibilities. The appendix contains notes on other systems, a list of institutions engaged in research with soilless culture, and a bibliography of some 70 references. The author concludes:

Given proper support, the writer feels that we may all confidently look forward to that not far distant day when there will be a hydroponicum in every home, banishing want, bringing economic independence and ensuring that the children of the future may grow up amid healthy surroundings with clean, fresh food to eat. Only then can weakness be overcome, and Indians grasp firmly that Freedom which has so recently been won.

The Nature and Properties of Soils. Fifth Edition. By T. LYTTLETON LYON, HARRY O. BUCKMAN, AND NYLE C. BRADY. The Macmillan Company, New York, 1952. Pp. 591. Price \$5.75.

A new name, Nyle C. Brady, has been added to the authors of this latest edition of what has long been recognized as probably the most complete text book in its field. All but five of the original 19 chapters have been revised or completely rewritten, and an additional chapter has been added. The presentation has been greatly improved by addition of much new material, including many excellent illustrations. Many references are given to show the origin of data and concepts. A simpler style of writing makes for much easier reading and better understanding by the student. The book is entitled to continued wide use in introductory courses in soils the country over.

Oxidation Potentials. Second Edition. By WENDELL M. LATIMER. Prentice-Hall, Inc., New York, 1952. Pp. 392. Price \$10.

This volume extends the thermodynamic data of the first edition. Heats of formation, free energies, and entropies are tabulated for all the more important inorganic compounds. The first two chapters have to do with units, conventions, and methods for determining oxidation-reduction potentials and with ionization potentials, electron affinities, and lattice energies in relation thereto. The remaining 21 chapters are concerned with the oxidation states of hydrogen and of the several groups of elements, arranged in accordance with their properties. References are shown for all values employed. The appendix gives a summary of oxidation-reduction potentials, activities of strong electrolytes, estimation of entropy values, and 40 study questions. The material assembled in this volume should be of great interest and value to physical chemists and plant physiologists who are concerned with soil-plant problems.

Phosphoric Acid, Phosphates, and Phosphatic Fertilizers. Second Edition. By WILLIAM H. WAGGAMAN. Reinhold Publishing Corporation, New York, 1952. Pp. 683. Price \$15.

The author is senior mineral technologist, Bureau of Mines, U. S. Department of Interior. The book is one of the American Chemical Society monograph series. The first edition was published in 1927, but developments in this field have been so rapid that virtual rewriting of the book was necessary. It is designed primarily for those who are engaged in the manufacture of soluble phosphates, but it should be of great interest and value to all those who are concerned in any manner with the fertilizer industry. The 29 chapters begin with a discussion of phosphorus in plant and animal life. This is followed by detailed consideration of the forms and sources of the element, the methods of manufacture of soluble forms, and the use of phosphates as fertilizers, leavening agents, cleansers, purifying agents, flame resisters, and a variety of other purposes. The appendix contains sets of very useful conversion factors, official methods of analysis, and numbers for some 3,000 patents, with patentees. The author has had the assistance of a number of men who have written chapters on their special fields. This is the most important book in its field.

Quantitative Chemical Analysis. By CHARLES W. FOULK, HARVEY V. MOYER, AND WILLIAM M. MACNEVIN. McGraw-Hill Book Company, New York, 1952.

The senior author of this book, now a professor emeritus, has long been recognized as an outstanding analytical chemist. His two colleagues have added the modern touch that was required to bring the original "Introductory Notes on Quantitative Analysis" up to date. The method of presentation is that of first outlining the theories involved in analytical procedures and then providing 33 exercises to which the procedures can be applied. The appendix lists equipment, special chemicals, standard substances, and materials for lecture demonstrations, ionization constants of weak acids and bases, solubility products of precipitates, densities of air and water, specific gravities of liquids, derivation of the Nernst equation, and signs of electrode potentials. The book is well illustrated with drawings, and the material is presented in readily understandable form. This is a first-class presentation of the subject.

Resources for Freedom. The President's Materials Policy Commission. U. S. Printing Office, Washington, D. C., 1952. Pp. 819. Paper-bound.

The five volumes that make up this report have to do with foundations for growth and security, outlook for key commodities, outlook for energy resources, promise of technology, and selected reports. The last report is concerned with mining laws, incentives for mineral industries, taxation of Canadian mineral industries, domestic and foreign forest resources, future demands on land productivity, fertilizer resources, water resources, Venezuelan petroleum, U. S. investments abroad, loans, government contracts, and stockpiling materials for security. A great deal of highly useful information is summarized in this report.

THE EDITORS

SOIL SCIENCE

VOLUME 74

November 1952

NUMBER 5

MOVEMENT OF WATER IN SOIL DUE TO A TEMPERATURE GRADIENT

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Received for publication February 9, 1952

The movement of water in sealed soil columns in the direction of high to low temperatures was first demonstrated by Bouyoucos (4) and confirmed in greater detail by Smith (15, 16), Maclean and Gwatkin (9), and Croney and Coleman (5). In all cases it was found that there was, for each soil, an optimum initial water content for maximum transfer of water, with little movement taking place in very wet or dry soils. The gradient of soil water content induced by the temperature gradient reached a steady value within a few days (9). The magnitude of the soil water gradient was found to be dependent on initial water content, bulk density, temperature gradient, and mean temperature.

Various hypotheses have been advanced for the mechanism of this transfer. Bouyoucos found that when the soil column was divided into two parts by an air space, across which the temperature gradient was applied, much smaller quantities of water were transferred than in a continuous column. He concluded that the flow must take place largely in the liquid phase, and gave a qualitative explanation of the flow being caused by change of water affinity of soil with temperature. Smith (15) has criticized Bouyoucos' findings on the basis that the temperature gradient in the latter's experiments affected only a small part of the soil column, which could account for the small water movement observed. On the grounds that the effect of temperature on the surface tension of water is not great enough to cause the observed water transfer, Smith suggested that transfer took place by means of vapor convection. This mechanism was also proposed by Maclean and Gwatkin (9), who assumed that equilibrium conditions were reached when the water content gradient became such as to give uniform vapor pressure throughout the soil. They gave no vapor pressure data to support this statement.

Smith (16), in a later paper, abandoned his theory of vapor movement, and proposed a mechanism of liquid flow, from the hot to the cold ends, initiated by small amounts of vapor condensation in capillary pores. Subsequently, Winterkorn (17) developed a theory of film flow of liquid water from the hot to the cold ends, along the internal surface of the porous soil system, due to change in water affinity with change in temperature. He considered this to be a more important mechanism than vapor movement. He also observed an electric potential differ-

¹ The work described in this paper was carried out as part of the research program of the Division of Soils, C.S.I.R.O., Australia, at the Waite Institute, Adelaide, South Australia.

ence in the soil due to the temperature gradient and suggested that the thermal water movement may be a special case of electro-osmosis.

The present paper reports an attempt to assess the contribution of liquid and vapor flow to the temperature effect by measuring changes in the distribution of a small amount of soluble salt in the soil. It is assumed that movements of soluble salts are due to transport in the liquid phase only.

METHODS

A "Perspex" cylinder, 10 cm. long and 14 cm. in internal diameter, was used to hold the soil. On one end was bolted a heavy brass plate to which was attached a flat circular electric heater. On the other end was bolted another brass plate forming one face of a cylindrical water chamber through which cold water could be pumped. The temperature of these faces was measured by thermistors

TABLE 1
Temperatures in soil columns at conclusion of runs

SOIL COLUMN		INITIAL WATER CONTENT	BULK DENSITY	TEMPERATURE AT DISTANCES FROM COLD FACE					
				0 cm.	2 cm.	4 cm.	6 cm.	8 cm.	10 cm.
		<i>per cent</i>	<i>gm./ml.</i>	<i>°C.</i>	<i>°C.</i>	<i>°C.</i>	<i>°C.</i>	<i>°C.</i>	<i>°C.</i>
Loam soil	A	1.7	1.59	9.5	—	15.8	—	22.2	26.0
	B	4.3	1.46	9.4	—	14.0	—	—	26.0
	C	5.3	1.40	9.5	—	14.5	—	21.6	26.3
	D	7.9	—	9.3	—	—	17.9	21.1	26.3
	E	9.6	—	9.4	12.5	16.2	—	21.7	26.0
	F	12.8	—	9.5	12.5	16.4	18.7	21.9	25.1
	G	14.3	—	9.5	13.1	16.4	18.5	21.6	24.8
	H	16.0	—	9.6	12.5	15.5	17.6	20.7	24.3
	J	19.8	—	9.7	12.5	—	17.1	20.8	25.1
	K	24.5	—	10.0	—	15.8	—	21.3	24.6
In figure 3		11.3	—	9.7	13.9	17.1	20.1	23.1	27.4
Washed fine sand	A	5.8	1.43	9.9	—	—	—	—	25.0
	B	7.9	1.45	9.9	—	—	—	—	25.0

soldered to each face. Holes were drilled in the side of the "Perspex" cylinder to allow the insertion of four thermistors at intervals of 2 cm. to measure the temperature gradient along the soil column.

In each experiment, the cold face was first bolted to the cylinder, the joint being sealed by a rubber gasket and rubber cement. The soil, which had been previously wetted as uniformly as possible and allowed to stand in a sealed can for at least a week, was firmly compacted in several layers into the cylinder, five samples being taken at the same time for determining the initial water and salt content. When the whole cylinder had been filled, the hot plate was attached and sealed in the same manner as the cold. Bulk density was determined at this stage on some of the columns (table 1). The thermistors were then inserted into the soil column, and the apparatus was placed horizontally in a constant temperature cabinet at 20°C. The thermistor leads were connected through a multiple switch to a resistance bridge, and the cold water pump and electric heater were then set going to establish a temperature of approximately 10°C. at the

cold face and 25°C. at the hot face. At the end of a run, the final temperature distribution was determined. The results, as given in table 1, show that the temperature gradient approximated 1.6°C. per centimeter.

After the apparatus was dismantled, the soil column was sampled in layers normal to the length of the column, each layer providing triplicate samples of approximately 35 gm. The distances of the midpoints of these layers from the cold face are recorded in figures 2, 3, and 4. The columns were divided into more layers in the later than in the earlier runs. Water contents of the triplicate samples were determined by oven-drying at 105°C., results being expressed as a percentage of weight of oven-dry soil. The same samples were then transferred to 75 ml. of distilled water and shaken for 1 hour. An index of the content of total soluble salts was obtained by measuring the electrical conductivity of this suspension, and the chloride content was determined by the electrometric titration of Best (2). The data used for construction of figures 2, 3, and 4 are the means of the triplicate determinations. Results of the electrical conductivity measurements which at low concentrations are influenced by factors other than soluble salts have not been given. They did, however, show the same trend as the more absolute determinations of chloride ions. Since chloride content was not determined for the earliest runs (fig. 2E and F and fig. 3), it was obtained indirectly from the electrical conductivity in these three cases by interpolation from a curve drawn through all the present experimental data relating these two quantities. Thus the chloride values in figure 2E and F and in figure 3 are not so accurate as those obtained directly by titration.

For some reason probably associated with the technique of raising the water content of the soil from air-dry condition to that of the columns, the chloride content of the initial samples of the loam soil was not uniform, the individual determinations obtained by titration having a standard deviation of 0.0062 me. per 100 gm. soil, whereas the mean value for each column ranged from 0.13 to 0.15 me. per 100 gm. soil. The standard deviation of individual determinations of the final chloride content of this soil was 0.0048 me. per 100 gm. soil, and to be significant at 5 per cent level the difference between mean values for chloride content must be at least 0.01 me. per 100 gm. soil.

The two soils used in these tests were sample 7800 of the A horizon of Urrbrae loam, and a fine sand which was obtained from sample 6349 of the A horizon of Holder fine sand after acid treatment, decantation to remove particles less than 0.02 mm., and washing to remove soluble salts. Some physical properties of these two soils are listed in table 2. Sodium chloride was subsequently added to the washed fine sand; the loam soil was used without addition of salt.

A guide to the degree of wetting represented by the water contents reported is given in figure 1, where the pF of the soil water at 20°C. is given as a function of water content for the two soils. The term pF is defined by Schofield (14) as the logarithm of the free energy difference between soil water and a free pure water surface at the same temperature, where the free energy is expressed as the height in centimeters of a water column above the free water surface needed to give the same free energy difference. The pF values of figure 1 derived from vapor pressure and freezing point depression measurements include the osmotic

component of the free energy difference, which does not, however, appear in the pressure membrane and tensiometer measurements. The discussion of the experimental results is concerned primarily with the range of water contents covered by the pressure membrane apparatus of Richards (13), and it is appro-

TABLE 2
Some properties of Urrbrae loam and washed Holder fine sand

	LOAM SOIL	WASHED FINE SAND
Particle size distribution		
{ 2-0.2 mm. %	1.9	20.0
{ 0.2-0.02 mm. %	50.2	80.0
{ 0.02-0.002 mm. %	31.3	0.0
{ <0.002 mm. %	16.6	0.0
Total soluble salts. %	0.077	—
Chloride content per 100 gm. soil. me.	0.14	—
Moisture equivalent. %	20.0	2.5
Permanent wilting percentage. %	6.3	—
Plastic limit. %	15.8	—

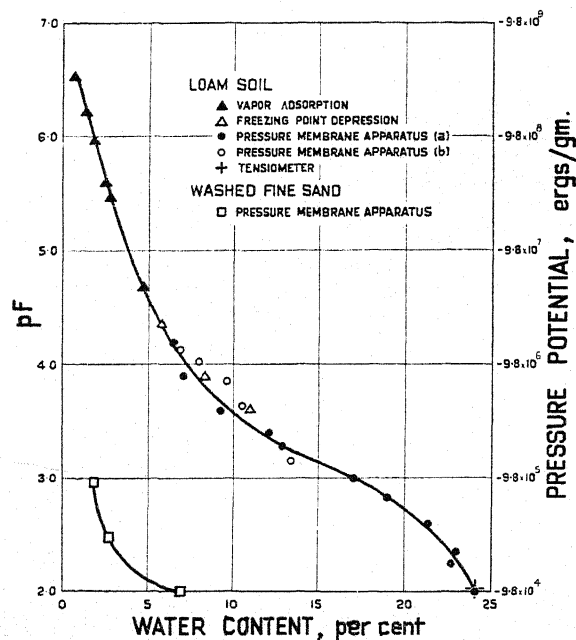


FIG. 1. RELATION OF pF, PRESSURE POTENTIAL, AND WATER CONTENT AT 20°C. FOR URRBRAE LOAM SAMPLES AND A WASHED FINE SAND

priate to discuss the data in terms of the hydrostatic pressure of the soil water. Accordingly, the equivalent values of pressure potential are also shown in figure 1, although limitations to the use of the term in the drier range are recognized. The pressure potential (3) represents the work done against the hydrostatic pressure forces in moving unit mass of water from a free water surface to the point in question, and is negative in unsaturated soils.

The data from the pressure membrane apparatus marked "a" in figure 1 are for sample 7800 as used in the present work (1). The remaining data for the loam soil were obtained from a similar but not identical sample of Urrbrae loam. Data from the pressure membrane apparatus marked "b" in figure 1 are for selected small aggregates (12). All pressure membrane, freezing point (8), and tensiometer (10) data are for soil drying out, but the vapor pressure data (12) are for soil becoming wet. Since both wetting and drying conditions are represented in the experimental data, use of figure 1 in relation to these data is limited by possible hysteresis in the free-energy-water-content relation.

RESULTS

The distribution of chlorides and water, 5 days after application of the temperature gradient to an initially uniform loam soil, is shown in figure 2. Ten columns

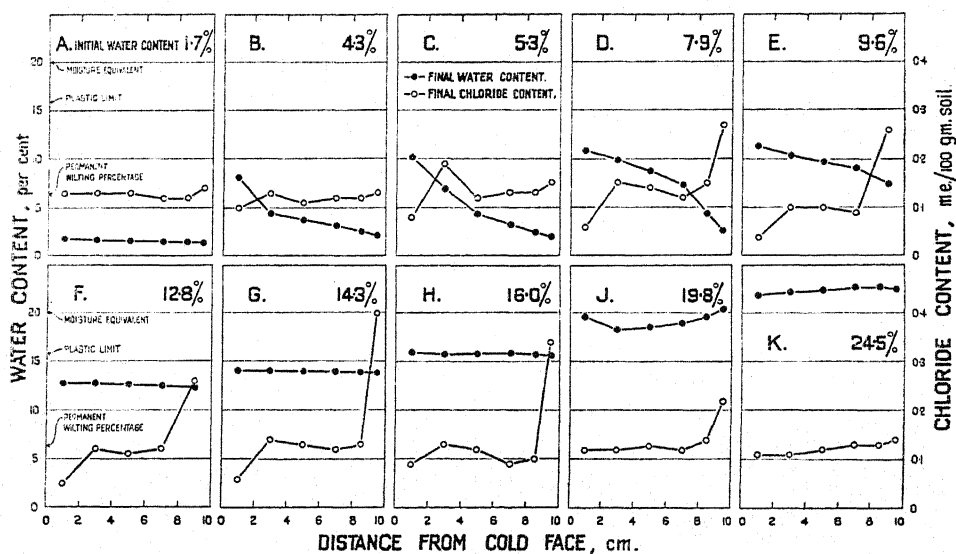


FIG. 2. DISTRIBUTION OF WATER AND CHLORIDES IN COLUMNS OF LOAM SOIL, OF VARYING INITIAL WATER CONTENTS, SUBJECTED TO A TEMPERATURE GRADIENT FOR 5 DAYS

A to K with initial water contents ranging from 1.7 per cent to 24.5 per cent are represented. In all except the wettest and driest cases, there has been a transfer of water toward the colder end of the columns and of chlorides toward the hotter end. This indicates that vapor transfer has occurred in the direction of decreasing temperature and that liquid (carrying salts in solution) has been transferred in the direction of increasing temperature. The transfer of chlorides is especially marked in figure 3, in which data are given from a longer run of 18 days with the loam soil.

The maximum transfer of water from the hot to the cold end in the 5-day period is found in columns C and D, which had initial water contents of 5.3 per cent and 7.9 per cent respectively. These two water contents have a mean value which is equal to one third of the moisture equivalent of this soil and they

correspond to pressure potentials of -3.0×10^7 and -0.8×10^7 ergs/gm. and to pF values of 4.5 and 3.9. In these two columns the water content has been reduced to about 2 per cent at the hot end and increased to more than 10 per cent at the cold end. When the columns were wetter or drier than these two, the amount of water transferred was less. This effect of initial water content on final distribution of water is in accord with that found by other workers (4, 5, 9, 15, 16). It appears, however, from the present interpretation that the figures represent a net rather than an absolute transfer of water, resulting from liquid and vapor movement in opposing directions. The changing shape of the water content curve in the successively wetter columns is then associated with increasing permeability of the system for liquid water and decreasing permeability for vapor.

It can be seen by reference to figure 1 that, except for minor anomalies in figures 2J and 2K, resulting probably from difficulty in packing very wet soil,

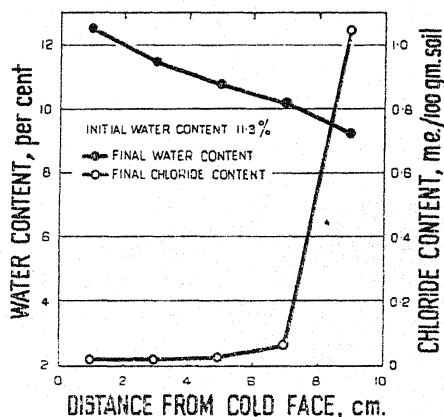


FIG. 3. DISTRIBUTION OF WATER AND CHLORIDES IN A COLUMN OF LOAM SOIL, OF 11.3 PER CENT INITIAL WATER CONTENT, SUBJECTED TO A TEMPERATURE GRADIENT FOR 18 DAYS.

there is a general gradient in the pressure potential of the liquid which favors movement from the cold toward the hot end. The gradient is numerically high in columns A, B, C, D, and E. Although it has lower values in columns F, G, and H, nevertheless, even in these cases there is a favorable gradient of 3,000 ergs/gm./cm. after allowance has been made for the effect of temperature on surface tension. This value is only approximate because of the limitations to the use of the curve of figure 1 already discussed.

The observed gradients in pressure potential can account for the flow of liquid water from the cold toward the hot end. A temperature gradient in a soil of uniform water and salt content gives rise, however, to a gradient of osmotic potential, which, if the soil could behave in effect as a semipermeable membrane, could also cause a flow of water in the direction cold to hot. The fact that the salts become more concentrated in time at the hot end also sets up an osmotic potential gradient favoring liquid movement to the hot end. To examine this, an osmotic

potential gradient was established favoring liquid flow in the direction hot to cold, that is, the reverse of that observed in the loam soil. Two columns (fig. 4A and B) of the washed fine sand previously described were used. A thin layer of sand, 2-3 mm. thick, of the same initial water content as the remainder of the sand but containing 7.2 me. NaCl per 100 gm. was placed immediately adjacent to the cold face. The chloride content of the remainder of the column was <0.01 me./100 gm. in column A and 0.03 in column B. The results given in figure 4 show that movements of the same type as for the loam soil took place, resulting in a net transfer of water to the cold end, and of salts toward the hot end. This shows that liquid moved toward the hot end irrespective of the direction of the osmotic potential gradient.

Variable salt concentrations will of course affect the vapor pressure and hence the movement of vapor, but these effects are of only a minor order in the present experiments in comparison with the effect of temperature on vapor pressure.

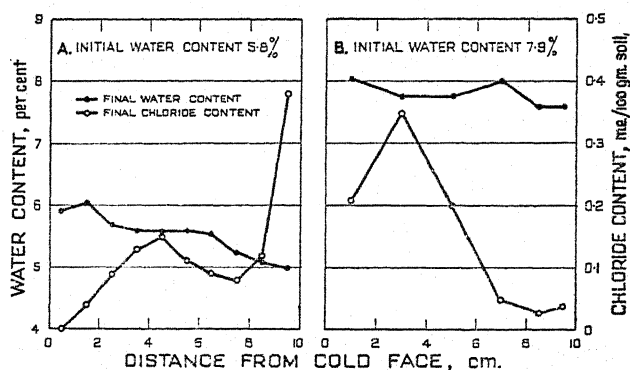


FIG. 4. DISTRIBUTION OF WATER AND CHLORIDES IN TWO COLUMNS OF WASHED FINE SAND (TO WHICH NaCl WAS INITIALLY ADDED AT THE COLD END) AFTER BEING SUBJECTED TO A TEMPERATURE GRADIENT FOR 10 DAYS.

There is evidence from the movement of chlorides in the loam soil that water movement in the liquid phase has occurred under surprisingly dry conditions. For example, in column D, chlorides moved toward the hot end of the column in soil which at no stage contained more than 7.9 per cent of water. Similarly in column C, movement occurred away from the cold end in soil which, near the point of peak concentration of chloride, can barely have reached that water content. The corresponding pressure potential for this soil is approximately -0.8×10^7 ergs/gm., which is equivalent to a pF of 3.9. It is of considerable interest that appreciable movement of water as a liquid occurred in soil as dry as this. The use of soluble salts or other tracers in this way appears to offer some promise as a tool for distinguishing between liquid and vapor flow in soils.

DISCUSSION

On the assumption that the observed movements of soluble salts are due to transport by water in the liquid phase, it would appear that liquid flow is in the

direction of cold to hot. The net movement of water in the opposite direction must then be attributed to a vapor flow in the direction of hot to cold and of greater magnitude at first than the liquid flow. The mechanism of water movement, therefore, is one in which the temperature gradient induces a flow of water vapor, which, on condensing in the cooler parts of the soil, increases the pressure in the soil water and causes liquid flow in the direction opposite to that of vapor flow. Liquid flow will proceed as far in that direction as permitted by the existence of conducting films.

In the discussion of this mechanism, it will be assumed that the rates of flow of liquid and vapor in the horizontal columns are proportional to the pressure gradients in the liquid and vapor respectively. The effect of temperature on these gradients may then be considered.

In an unsaturated soil, water is at a hydrostatic pressure P which is negative with respect to that at a free flat water surface and is given (7) by

$$P = \frac{2S}{r} \quad (1)$$

where S = surface tension of water and r = radius of curvature of the liquid surface in the soil pores.

Since S decreases with increasing temperature, and r is assumed to have a constant negative value, P will increase with increasing temperature. Consequently if a temperature gradient is established in a uniform soil of uniform water content, a pressure gradient will result, tending to move liquid water in the direction of decreasing temperature.

There will be a similar tendency for water vapor to flow in the same direction, since it may be assumed that the vapor pressure of the soil water, p , will increase with temperature as in the case of the vapor pressure of free water, p_0 . (For soils no drier than the permanent wilting percentage, it is probably true that at any given temperature $1 > \frac{p}{p_0} > 0.98$ over the range of temperature under consideration.)

Although water will at first move in the direction of decreasing temperature in both the liquid and vapor phases, it can be shown that this condition of flow may be temporary only. At the end of what may be termed a first stage in adjustment of water to a temperature gradient, sufficient movement will have taken place to remove the gradient in P in the liquid phase. If it is assumed that there is no effect from soluble salts, the relation of p to T at this stage may be considered (7) through the equation:

$$P = \rho RT \log \frac{p}{p_0} \quad (2)$$

$$\text{or} \quad \log p = \log p_0 + \frac{P}{\rho RT} \quad (3)$$

where T = absolute temperature, R = gas constant per gram of water, and ρ = density of water.

Any increase in T will cause an increase in p_0 and, with P constant and negligible changes in ρ disregarded, $\frac{P}{\rho RT}$ will become a smaller negative quantity.

Hence, according to equation (3), p will increase with temperature and there will be a tendency for vapor to flow even when the water in the system is so adjusted that there is no longer a tendency for liquid to do so.

Suppose the movement of vapor in the direction of decreasing temperature to be continued further until, as a result of evaporation and condensation, a condition of vapor pressure equilibrium is reached. The relation of P to T under such circumstances can be examined by means of equation (2) in which p is now taken as constant. Since p_0 increases with T and $\log \frac{p}{p_0}$ is negative, it follows that P will decrease with increasing values of T . Hence, liquid water will tend to flow in the direction of increasing temperature—a direction which is the reverse of that during the first stage of adjustment.

Gains or losses of water affect the vapor pressure of soil water only slightly in a moist soil at constant temperature. Consequently, in a soil that is sufficiently moist to provide a connected conducting path for liquid water, this reversal in the direction of liquid flow will probably begin before the vapor pressure gradient and the rate of flow of vapor have decreased appreciably, thus preventing a condition of vapor pressure equilibrium. A circulating system will therefore operate in which vapor moves in the direction of decreasing temperature and liquid moves in the opposite direction as far as permitted by the presence of conducting water films. Within the closed system, flow in each direction will finally become equal and will be governed by the pressure gradients and the permeability for the liquid and vapor phases respectively. Where soluble salts are present, final equilibrium will also be affected by their distribution in the soil. For normal values of salt concentration, however, this effect appears to be small in comparison with the above effects.

To account for the observed movements of water, a rate of flow of vapor in excess of that calculated by Penman's diffusion equation (11) is required. From the observed net transfer of water in column C of figure 2, for example, it may be calculated that a vapor flow of 0.18 gm./sq. cm. took place in 5 days across the plane at which the initial water content remained unchanged. This value is an underestimate of the vapor flow because of reverse liquid flow, which, however, is small in this case. On the other hand, the vapor flow calculated by Penman's equation is only 0.05 gm./sq. cm. for the same period. This discrepancy warrants further investigation.

The effects of commonly occurring temperature gradients upon water movement in soils in the field are known to be appreciable (6), and it has been suggested that they may be of importance in certain engineering problems (5, 17). Certainly there is evidence in figure 2 of considerable movement of water, especially in the middle range of water contents. It should be stressed, however, that the present work was done in a closed system from which water loss was prevented and in which the temperature gradient was unaffected by the transfer

of latent heat. These limitations apply also to the remarkable salt movements noted in the present work.

SUMMARY

The effect of a temperature gradient on the movement and distribution of water in soil has been examined in closed columns of soil for a wide range of initial water contents. Small amounts of soluble salts acting as a tracer served to distinguish between liquid and vapor movement.

In all except the wettest and driest columns of soil, there was a transfer of water toward the colder end of the column and of salts toward the hotter end.

This result is considered to be due to a net transfer of water from hot to cold, in which water evaporating from the hotter soil moves as a vapor into colder soil, where it condenses and returns as a liquid when a favorable gradient of pressure potential has been established. It is shown from theoretical considerations that, when the soil is sufficiently wet to permit liquid flow, a state of equilibrium cannot be reached, and continuous circulation of the soil water takes place.

The maximum net transfer of water from the hot to the cold end occurred in columns the initial water contents of which were approximately one third of the moisture equivalent.

Movement of water in the liquid phase is shown to have occurred at a low water content, which corresponded to a pressure potential of -0.8×10^7 ergs/gm. (pF 3.9).

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RESPIRATION RATES AND PLATE COUNTS FOR DETERMINING EFFECT OF HERBICIDES ON HETEROTROPHIC SOIL MICROORGANISMS¹

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Received for publication October 31, 1951

Minarik (4) has observed that the persistence of pre-emergence herbicides is controlled primarily by leaching and secondly by microbial decomposition. The disappearance of 2,4-dichlorophenoxyacetic acid from the soil has been attributed by Audus (1) to a rather specific group of bacteria. The action on many other herbicides does not seem to be quite so specific (4).

A possible bacteriostatic action on certain of the soil bacteria by herbicides has also been noted. Smith, Dawson, and Wenzel (7) reported that 100 ppm. of 2,4-D inhibited the nitrifying bacteria but recovery occurred in 10 to 40 days. When 500 ppm. was used, the bacteria had not recovered after a 90-day period. Fults and Payne (3) have shown that 2,4-D in amounts as low as 0.009 pound per acre depressed nodulation of the common bean. Carlyle and Thorpe (2) noted that other species of *Rhizobium* may also be affected.

This paper reports the effect of herbicides on respiration rates and plate counts of soil microorganisms as determined in initial investigations of field plots that had previous herbicidal treatment.²

EXPERIMENTAL STUDIES

The method of Quastel and Scholefield (6) for measuring the respiration rates of the nitrifiers in an enriched soil with the Warburg apparatus was adapted to measure respiration rates of the heterotrophic microorganisms.

Soil samples from the 0-1-inch horizon were obtained from field plots treated with the following herbicides: dinitro-o-secondary butyl phenol (Dow General, 3 lbs./acre); 3(para-chlorophenyl) 1,1-dimethyl urea (DuPont CMU, 2 lbs./acre). ortho-chlorophenol-sulfonyl fluoride (Penn Salt NP-128, 20 lbs./acre); sodium 2,4-dichlorophenoxyethyl sulfate (Exper. Herb. I, 2 lbs./acre); and isopropyl-N-phenyl carbamate (IPC, 20 lbs./acre). The soil samples were obtained approximately 1 and 3 months after the field applications. The soil is classified as Grose-close silt loam.

The standard procedure usually followed in Warburg methods was employed. In each flask was placed 1½ gm. of soil to which was added 2 ml. of an aqueous

¹ This study was made possible by the support of the Virginia Polytechnic Institute Educational Foundation, Incorporated.

² Since the preparation of this report the authors have read with interest the article by D. E. Kratochvil published in volume 1, pages 25-31, of the new journal *Weeds*, October, 1951. The authors agree that the principle affords a reliable means of measuring the effect of a herbicide. The present paper is offered as a more convenient procedure of employing the manometric principle for measuring the effect of herbicides on the heterotrophic soil microflora.

solution of glucose and K_2HPO_4 . Control manometers were set up with the soil suspended in 2 ml. of water. Filter papers plus KOH were placed in the center walls, and the manometers were arranged for shaking. The experiment was carried out at $37^\circ C.$, and the manometers were read at the end of $2\frac{1}{2}$ hours. Preliminary experiments showed that $2\frac{1}{2}$ hours was sufficient time for the respiration rate to reach a maximum.

The results of the oxygen uptake of the soils collected at 1- and 3-month periods after the herbicide had been applied to the field plots are shown in table 1. Comparison of the difference in microliters of oxygen uptake with and without

TABLE 1
Typical oxygen uptake from soils after 1 month and 3 months of herbicidal treatment

TREATMENT OF SOIL	SUBSTANCE ADDED TO $1\frac{1}{2}$ GM. SOIL IN WARBURG FLASK	O ₂ UPTAKE*			
		Quantity		Difference due to glucose additions	
		1 month	3 months	1 month	3 months
No herbicide	Water†	$\mu l.$ 30.3	$\mu l.$ 34.0	$\mu l.$ 43.5	$\mu l.$ 22.9
	Glucose‡	73.8	56.9		
Sodium 2,4-dichlorophenoxyethyl sulfate (Exper. Herb. I)	Water	34.2	25.6	45.8	21.4
	Glucose	80.0	47.0		
3(para-chlorophenyl)-1,1-di- methyl urea (CMU)	Water	29.2	22.5	39.4	20.2
	Glucose	68.6	42.7		
Isopropyl-N-phenyl carbamate (IPC)	Water	29.0	24.9	51.4	22.0
	Glucose	80.4	46.9		
Ortho-chlorophenol-sulfonyl fluo- ride (NP-128)	Water	31.8	26.8	34.1	11.2
	Glucose	65.9	38.0		
Dinitro-o-secondary butyl phenol (Dow General)	Water	35.5	22.7	35.5	13.0
	Glucose	71.0	35.7		

* Maximum difference for duplicate analysis was approximately 5 microliters.

† 2 ml. water.

‡ 1 ml. 0.01 M glucose and 1 ml. 0.02 M K_2HPO_4 .

the addition of glucose indicates that the field applications of Dow General, DuPont CMU, and Penn Salt NP-128 may be inhibiting the respiration activity of the soil microflora after 1 month. Similarly, the Dow General and Penn Salt NP-128 may still have an inhibitory effect after the 3-month period. The Exper. Herb. I and IPC apparently did not reduce the respiration rates of the organisms at either sampling date. The differences in duplicate measurements of the respiration rates varied as much as 5 microliters of oxygen uptake. Dry weather may have been the cause of low respiration rates of the bacteria in all treatments at the second sampling date.

The usual method for determining the effect of a chemical treatment on the soil microflora is by plate counts. For a comparison of the results obtained by measuring respiration rates, the plating technique for counting the microflora was used. The soil samples were plated out on a soil extract agar containing glucose and K_2HPO_4 . The results are shown graphically in figure 1. The mean of eight plates plus or minus 3 times the probable error of the mean is shown. The use of $3 \times P.E.m$ gives odds of 22 to 1 that the true mean will be within this range.

The results of the plate counts show that the order of inhibition is almost identical with the inhibition of respiration rates except for IPC after the 1-month

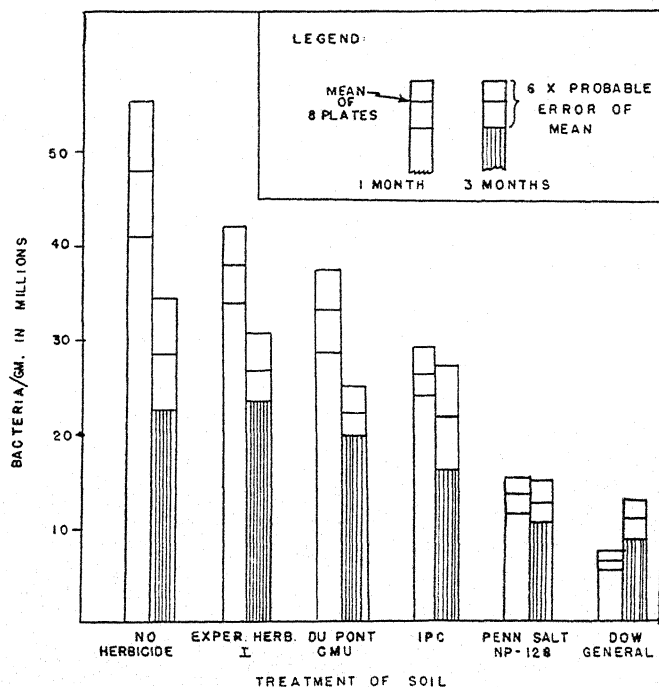


FIG. 1. ENUMERATION OF BACTERIA 1 MONTH AND 3 MONTHS AFTER HERBICIDE TREATMENT

period. The increase of the respiration rate of the bacteria in the soil sample treated with IPC above that of the control might support the contention of Newman, DeRose, and DeRigo (5) that this compound is readily decarboxylated.

SUMMARY

Manometric means for measuring the respiration of a soil sample were used as a convenient method to indicate inhibition of the heterotrophic soil microflora by certain herbicides. Enumerations of the bacteria by plate counts were shown to agree closely with the respiration rates. Under the conditions of this study, the results indicate that of the herbicides studied, Dow General and

Penn Salt NP-128 reduced the respiration rate and plate counts of the saprophytic microflora for 3 months after treatment. CMU showed a similar reduction for 1 month.

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ELECTROCHEMICAL PROPERTIES OF HYDROGEN CLAYS FROM INDIAN BLACK COTTON SOIL

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Received for publication September 10, 1951

Systematic studies have been made by Mukherjee and his co-workers (8, 9, 10, 11, 12, 13, 14) of the fundamental electrochemical character of hydrogen clays isolated from a number of Indian soils, kaolin, and bentonites, as revealed by their buffer capacities and the nature of their titration curves with bases, free and titrable acidity in absence and in presence of neutral salts, displacement of aluminum and iron by neutral salts, and variations in the viscosity of clay suspensions on addition of increasing amounts of alkalis. The mineralogical composition of these clays was also determined by x-ray, thermal, and optical methods and correlated with their electrochemical properties. Besides elucidating a number of points of considerable agronomic importance, the results of this comprehensive work show that the clay fractions isolated from Indian soils usually contain more than one clay mineral (that is, secondary aluminosilicate minerals) but generally kaolinite is the dominant mineral constituent of laterites and lateritic soils, whereas black cotton soils are predominantly montmorillonitic. The work was carried out mostly with surface soils.

It is well known that during the process of weathering and formation of soils, such factors as eluviation and illuviation of colloidal constituents and soluble salts, soil reaction, soil moisture, temperature, microbial activity, drainage conditions, and parent material have important effects on the nature and amount of clay minerals formed in different horizons of the profile. For instance, Nagelschmidt *et al.* (15) found that soils in India derived from granite and gneiss contained mainly kaolin under eluvial conditions and montmorillonite under illuvial conditions. Hosking (3) has shown that in Australia under conditions of abundant rainfall and active leaching, kaolinitic soils form from basic igneous rocks, whereas, under conditions of low rainfall and poor leaching, montmorillonite soils form from the same parent rocks. Kelley (4) in an analysis of a Susquehanna profile has found that kaolinite is present in the top 20 inches under strong acid leaching conditions, but that montmorillonite is present at the bottom of the profile. Some soils contain mixtures of clay minerals, but others have a single mineral as the dominant component. These are primarily mature soils in which the clay minerals have had sufficient time to develop. It has also been observed that in clays containing mainly kaolinite and some montmorillonite in the entire clay fraction, the latter mineral tends to be concentrated in the finer subfraction.

Systematic investigations on the electrochemical and mineralogical properties of Indian soils on a profile basis have been very few. Nagelschmidt *et al.* (15) made a comparative study of the physicochemical and mineralogical characters of soil samples from a black soil profile and from an adjacent red one from

Hyderabad. Raychaudhuri *et al.* (17) made a similar study of a black and a red soil profile from Coimbatore.

The purpose of the present investigation was to examine in detail the electrochemical and related properties of H-clays isolated from horizon samples of a typical black cotton soil (*regur*) profile from Indore, with a view to gaining fuller information on the development and genesis of these soils with special reference to the nature and distribution of clay minerals with depth.

MATERIALS AND METHODS

The profile

A description of the profile to a depth of 6 feet follows. As is to be expected for a soil of this type, the profile is more or less uniform, and the change from horizon to horizon is not sharp.

TABLE 1
Mechanical composition of a typical black cotton soil from Indore
Air-dry basis

HORIZON	MOISTURE	LOSS ON IGNITION	SAND	SILT	CLAY
<i>inch</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0-1½	7.6	7.6	27.2	22.5	35.6
1½-3	8.1	7.2	30.9	21.0	34.6
3-6	8.9	6.7	15.0	26.1	44.6
6-9	9.2	6.2	13.6	25.7	47.7
9-12	9.3	6.1	11.7	24.9	48.6
42-48	9.0	5.7	11.3	23.5	50.5
66-72	9.2	5.5	11.3	21.2	52.4

Location: F 42. Institute of Plant Industry, Indore, India.

Vegetation: Virgin land (grass strip).

0-24 inches: Friable, with roots of plants, black color, clayey loam.

24-42 inches: Semifriable, black color, clayey.

42-60 inches: Harder soil with very little disintegrated parent material, change in color to grayish black, clayey.

60-72 inches: Still harder soil with disintegrated parent material, clayey.

Samples were collected from the following horizon levels: 0-1½, 1½-3, 3-6, 6-9, 9-12, 18-21, 30-36, 42-48, 54-60, and 66-72 inches.

The results of the mechanical analyses of seven of the soil samples (table 1) show that the clay fraction increases with depth, from 35 per cent in the top layer to about 52 per cent at a depth of 72 inches. The sand fraction (coarse and fine composite) decreases correspondingly from 30 to about 11 per cent. This shows eluviation of fine clay from the upper to the lower horizon.

The soil is slightly alkaline, the pH varying between 7.3 and 7.6.

Separation of the clay fractions

The clay fractions ($<2 \mu$) were separated from horizon samples by dispersion in distilled water and siphoning off of the top 20 cm. of the suspension after 24

hours. The organic matter was removed from the clay fraction by exhaustive treatment with 6 per cent H_2O_2 . All exchangeable bases were then replaced by repeated leaching with 0.02 N HCl. The H-clay thus obtained was washed free of excess acid and dispersed in distilled water to obtain approximately 1 per cent clay in the suspension.

RESULTS AND DISCUSSION

Chemical composition of the hydrogen clays

The results of fusion analyses of the H-clays from different horizons of the profile are presented in table 2.

The silica-sesquioxide ratio in these H-clays is about 3, and this value is more or less maintained throughout the profile. As a consequence of the gradual

TABLE 2

Chemical composition of H-clays from a typical black cotton soil from Indore

HORIZON	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	$\text{SiO}_2/\text{R}_2\text{O}_3$	$\text{SiO}_2/\text{Al}_2\text{O}_3$
<i>inch</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		
1½-3	58.70	28.21	9.81	0.48	0.88	1.88	2.90	3.46
6-9	57.47	27.65	10.93	0.45	0.96	1.61	2.82	3.53
18-21	56.78	27.92	10.59	0.42	1.76	1.39	2.78	3.46
30-36	57.33	25.36	13.74	0.16	1.26	1.70	2.85	3.83
42-48	58.92	23.14	14.14	0.14	2.56	1.69	3.12	4.32
66-72	58.60	22.61	15.71	0.21	2.74	2.75	3.05	4.42

TABLE 3

CaO in H-clays from a typical black cotton soil from Indore

HORIZON	ORIGINAL CaO	AFTER HCl TREATMENT	AFTER ELECTRODIALYSIS
<i>inch</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
6-9	0.45	0.45	0.40
30-36	0.16	0.20	0.16

decrease in the percentage of Al_2O_3 , the silica-alumina ratio, however, slightly increases with depth. Appreciable amounts of nonexchangeable Mg and K are present. The presence of 1.4 to 2.7 per cent K_2O suggests that the clay minerals, which are mainly montmorillonitic as judged from their electrochemical properties, also contain some illite. The proportion of the latter amounts to 20 to 35 per cent, when calculated on the assumption that illite has essentially the same structure as montmorillonite with the exception that 15 per cent of the Si^{++++} has been replaced by Al^{+++} and the resulting negative charge is balanced by K^+ (2).

A trace of Ca—0.14 to 0.48 per cent CaO—is present in these H-clays. That this Ca is not in the exchangeable form is proved by failure of repeated leaching of these H-clays with dilute HCl and of exhaustive electrodialysis to remove the Ca. These results are shown in table 3.

The H-clays have dimensions of $2\ \mu$ or less, and it is not improbable that they contain traces of unweathered primary soil-forming minerals, for example, feldspar. Coleman and Jackson (1) in an analysis of H-clays ($<0.2\ \mu$) from Coastal Plain soils of southeastern U. S. A. also found Ca, varying between 0.8 and 1.5 per cent, which they attributed to the "presence of unidentified minerals or unorthodox types of lattice substitution." Kelley *et al.* (5) reported the presence of a small percentage of nonreplaceable Ca in some samples of Ca-saturated clay colloids ($<1\ \mu$) from California soils. Whether the Ca found in H-clays of the

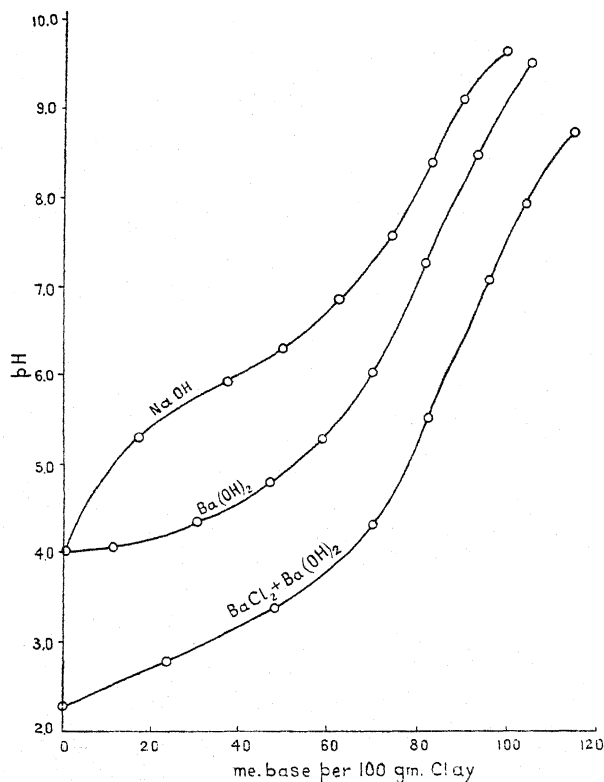


FIG. 1. TITRATION CURVES OF H-CLAYS FROM THE 9-12-INCH HORIZON OF A TYPICAL BLACK COTTON SOIL FROM INDORE

Indore black cotton soils originated from unweathered Ca-bearing minerals such as feldspar or is present in the lattice in nonexchangeable form is not clear.

Electrochemical properties

Potentiometric titrations of H-clays with NaOH and Ba(OH)₂ were carried out according to the method of Mukherjee (6, 7). The nature of the titration curves varies with the type of alkali used. Figure 1, which gives titration curves of H-clays from the 9-12-inch horizon with NaOH and Ba(OH)₂, both in absence

and in presence of $N \text{ BaCl}_2$, is a typical example and is characteristic of montmorillonite. The NaOH curve indicates a weak monobasic acid character. The inflection points for the different H-clays lie between pH 7.6 and 8.8. The $\text{Ba}(\text{OH})_2$ curve is characteristic of a strong monobasic acid with the inflection point between pH 6.6 and 7.7. In presence of $N \text{ BaCl}_2$, the baryta curve also shows a strong monobasic acid character, but the inflection occurs at a lower pH (between 5.9 and 7.1). The initial pH of all these H-clays lies between 4.05 and 4.45.

TABLE 4
Base-exchange capacity of H-clays from a typical black cotton soil from Indore

HORIZON	TITRATED WITH NaOH		TITRATED WITH $\text{Ba}(\text{OH})_2$		TITRATED WITH $\text{Ba}(\text{OH})_2$ IN PRESENCE OF $N \text{ BaCl}_2$	
	pH 7	Inflection	pH 7	Inflection	pH 7	Inflection
<i>inch</i>	<i>me.*</i>	<i>ml.</i>	<i>me.</i>	<i>ml.</i>	<i>me.</i>	<i>ml.</i>
0-1½	28.0	59.0 [8.6]†	46.5	54.0 [7.7]	72.5	73.0 [7.1]
1½-3	47.5	64.0 [8.5]	60.5	65.0 [7.5]	78.2	74.0 [6.5]
3-6	61.0	70.0 [7.8]	69.0	67.0 [6.7]	87.5	75.0 [5.5]
6-9	63.5	79.0 [8.4]	78.5	75.0 [6.6]	99.0	84.0 [5.4]
9-12	64.0	82.5 [8.4]	79.5	77.0 [6.7]	95.0	85.0 [5.9]
18-21	60.0	82.5 [8.3]	77.5	77.0 [6.3]	88.5	80.0 [6.0]
30-36	59.0	76.0 [8.4]	74.0	76.0 [7.3]	96.5	90.0 [6.1]
42-48	65.0	74.0 [7.6]	79.5	80.0 [7.1]	95.5	90.0 [6.4]
54-60	68.0	74.0 [7.8]	78.5	76.0 [6.6]	98.5	92.0 [6.3]
66-72	63.0	87.0 [8.8]	86.0	88.0 [7.4]	97.5	95.0 [6.7]

* me. = per 100 gm.

† Figures in brackets indicate pH values at inflection points.

TABLE 5
Base-exchange capacity of H-clays from a typical black cotton soil from Indore as determined by different methods

METHOD	BASE-EXCHANGE CAPACITY
	<i>me./100 gm.</i>
Schollenberger (with $N \text{ NH}_4\text{OAc}$, pH 7).....	87.0
Parker (with $N \text{ BaOAc}$, pH 7).....	89.3
Titration with baryta in presence of $N \text{ BaCl}_2$	89.0

The base-exchange capacities of H-clays as calculated at pH 7.0 and at the inflection points in the titration curves with NaOH and $\text{Ba}(\text{OH})_2$ are recorded in table 4.

It will be noticed that the base-exchange capacities calculated at the inflection points and also at pH 7.0 show irregular variations in some cases but, with a few exceptions, they do not appear to differ greatly with depth. The high base-exchange capacity, the nature of the titration curves, and also the pH values at the inflection points suggest that the dominant mineral present in these H-clays belongs to the montmorillonite group (11).

The base-exchange capacities of these clays were also determined by Scholtenberger's (18) and Parker's (16) methods. The values were found to be almost identical with those obtained by potentiometric titration with baryta in presence

TABLE 6
Effect of increasing base saturation on viscosity of H-clay suspensions from a typical black cotton soil from Indore

HORIZON	INITIAL VISCOSITY	MAXIMUM VISCOSITY	INCREASE IN VISCOSITY	NEUTRALIZATION AT MAXIMUM VISCOSITY
<i>inch</i>	<i>centipoise</i>	<i>centipoise</i>	<i>centipoise</i>	<i>per cent</i>
1½-3	.816	0.957	.141	68.8
6-9	.791	1.005	.214	60.8
18-21	.790	0.954	.164	60.0
30-36	.785	0.985	.200	67.8
42-48	.792	0.969	.177	62.2
66-72	.764	0.943	.179	63.2

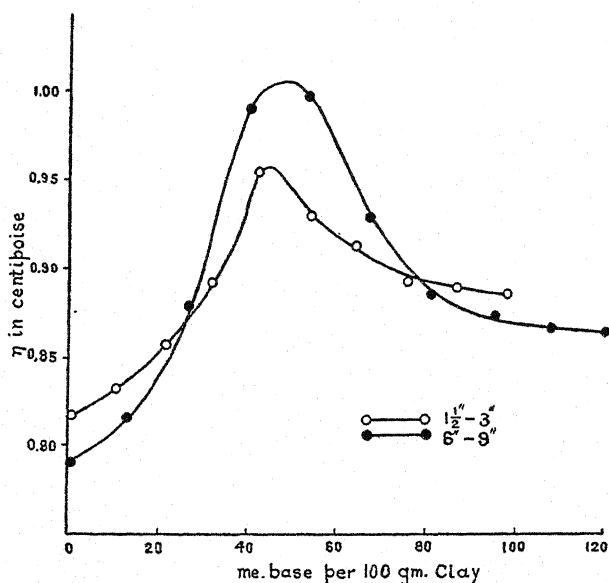


FIG. 2. EFFECT OF INCREASING BASE SATURATION ON VISCOSITY OF H-CLAY SUSPENSIONS FROM A TYPICAL BLACK COTTON SOIL FROM INDORE

of $N BaCl_2$ (table 5). This suggests that with a normal salt concentration and at pH 7, the difference in the effects of NH_4^+ and Ba^{++} practically vanishes.

Electroviscous properties

The montmorillonitic nature of the clays was further confirmed by viscosity studies of the suspensions (11). Like pure montmorillonite, the viscosity of an 0.88 per cent H-clay suspension with increasing addition of NaOH was found to

increase steadily, reach a maximum value at a point between 60 and 68 per cent neutralization, and then decrease gradually. The results obtained with six of the samples along the profile are given in table 6. Figure 2 illustrates the viscosity curves of H-clays from two horizons; other hydrogen clays produce exactly similar curves.

Thermal dehydration

Thermal dehydration studies by the method of Kelley *et al.* (4) further elucidated the nature of the clay minerals. The nature of the thermal dehydration

TABLE 7

Thermal dehydration of H-clays from a typical black cotton soil from Indore

HORIZON	TOTAL WATER	ADSORBED WATER	LATTICE WATER	INFLECTION TEMPERATURE
inch	per cent	per cent	per cent	°C.
1½-3	15.2	11.2	4.0	410
6-9	15.6	11.0	4.6	400
18-21	16.6	12.5	3.9	440

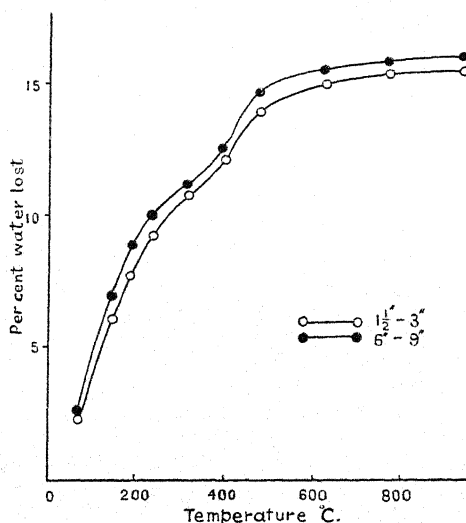


FIG. 3. THERMAL DEHYDRATION CURVES OF H-CLAYS FROM A TYPICAL BLACK COTTON SOIL FROM INDORE

curves (high adsorbed water as compared to crystal lattice water, and the inflection temperature) shows that the dominant mineral in these clays belongs to the montmorillonite group (table 7 and fig. 3).

SUMMARY

Electrochemical and related properties of hydrogen clays prepared from horizon samples of a typical black cotton soil (*regur*) from Indore were studied. Data have been presented on the chemical composition, electrochemical and

electroviscous properties, and thermal dehydration studies of these clays. Montmorillonite was found to be the predominant mineral; some illite was present, to the extent of 20 to 35 per cent. The electrochemical properties of the clays showed very little change with increasing depth.

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VARIATIONS IN SOIL BORON WITH CULTIVATION AND SEASON

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Received for publication January 14, 1952

Certain climatic factors appear to have a definite influence upon the amount of boron translocated from soil to plant. The effect of dry weather in preventing plant uptake of boron was shown by Walker (5), who reported that well-fertilized beets in the Racine-Kenosha area of Wisconsin which had received an application of 75 pounds of borax per acre made rapid growth until about half grown, when almost no rain fell for 4 weeks. Near the end of this period and about 2 weeks before harvest, internal black rot (boron deficiency) appeared, affecting 25 per cent of the crop. Latimer (3) found that high summer temperature and various other climatic conditions were not correlated with internal cork (boron deficiency) of apples in New Hampshire, but that drought in June and July was the most important predisposing factor to this disease. The effect of temperature in releasing boron from soil was studied by Eaton and Wilcox (2), who found that in the range 6 to 35°C. the amount of boron liberated by 1-to-1 suspensions in 0.005 N CaSO_4 solution rose from 1.40 to 2.18 ppm. As this temperature range is ordinarily experienced in the production of economic crops, it would seem that a similar release of boron might occur under field conditions.

Effect of climatic changes in a cultivated soil upon amount of boron determined in subsequently air-dried samples was first noted in 1945. Seasonal effects, shown in table 1, were difficult to evaluate because of parallel variations in temperature and rainfall. The purpose of the present investigation was to study the effects of prolonged cultivation and diverse seasonal changes upon the amounts of boiling-water-extractable boron in certain Florida soils.

MATERIALS AND METHODS

De Turk and Olson reported (1), "Although the water-soluble fraction is not an exact index of the boron in the soil available to the plant, yet this portion is probably a truer measure of the available form than either the acid-soluble fraction or the total." Rogers (4) who investigated several extraction methods for soils within the boron range 0.03 to 0.22 ppm., pointed out that though a hot-water-extraction procedure gave satisfactory results with coarse-textured red and yellow podzolic soils of Alabama, the critical values thus established probably would not apply to fine-textured soils of the same region or soils of other regions that have high boron-fixing capacities. The boiling-water extraction procedure was considered suitable for the present study, however, because all the soils were of similar texture and because comparisons were to be made for successive samplings at each location, with climatic factors as the variable. An extraction period of 5 minutes of boiling was used (6), and differences in

¹ Florida Agricultural Experiment Station Journal Series No. 54.

colorimetric values from duplicate aliquots usually were within plus or minus 5 per cent. Duplicate extractions, where used, showed similarly close agreement.

The seasonal conditions sought for sampling the soils were: winter dry, summer dry, and summer wet. The first group of samples was taken in January, 1950, an extremely dry period; the second group in June, 1951, which was hot and dry; and the third group in August, 1951, which was hot and wet. The rainfall for one month prior to each sampling was, respectively, 0.37, 1.08, and 12.56 inches. Winter rains usually are brought about by cold fronts from the northwest, but as the January, 1950, sampling period was almost without rain, it was warmer than usual, with an average maximum air temperature of 80.3°F. and an average minimum of 55.5°. The averages for the month prior were maximum 74.2° and minimum 50.5°, and for November, 1949, they were maximum 73.3° and minimum 48.6°. Thus, though air temperatures at time of sampling in January were high, these soils had been exposed for a prolonged period to cool weather, with temperatures in the November-December period dropping nine times to as low as 34 to 39°. In contrast, temperatures for June, 1951, averaged 92.3° maximum and 69.6° minimum; and for August, 1951, 93.7° maximum and 72.5° minimum. These records were from the weather station at Gainesville, which is centrally located in the area sampled.

The upland mineral soils in this study are well-distributed in Alachua County, Florida, and each sampling position was selected because it offered an opportunity to contrast a soil under prolonged cultivation with the immediately adjoining virgin soil. All samples were taken, in the 0-6-inch depth, with a stainless steel sampling tube $1\frac{3}{8}$ inches in diameter. About 12 plugs were obtained at each location to ensure a representative sample. The soils were spread on Kraft paper at room temperature until completely air-dried. All samples were then sifted three times through a 2-mm. perforated aluminum sieve, mixed until thoroughly homogenized, and stored in cardboard ice cream cartons until analyzed. Each group of soils was analyzed for boron within 2 to 5 months after it was sampled. Previous analysis of similar unsupplemented soil showed no effect of storage time on the amount of boron determined. The pH values, obtained on all soils of the August, 1951, sampling, were determined as soon as the soils had completely air-dried.

RESULTS

The reaction in Arredondo loamy fine sand (table 1) averaged about pH 5.7, and the range for all soil types in table 2 was from pH 5.08 to 6.09. Reaction appears not to have influenced the boron values in any of these studies.

Though the data in table 1 are limited, they are fundamental to the understanding of seasonal variations in boron. In this shallow phase of Arredondo loamy fine sand where clay is only 12 to 18 inches from the surface, the behavior of boron throughout the summer rainy season was of definite interest. Since rainfall for the 3 days prior to each sampling period was extremely high, ranging from 1.59 to 5.52 inches, the constancy of the value for boiling-water-extractable boron at 0.17 ppm. seems remarkable. Conservation of native boron

in these instances is believed to have resulted from colloids in the topsoil, plus the proximity of the fairly stiff clay in the subsoil. Such losses as may have occurred by leaching perhaps were compensated by progressive liberation of boron from the mineral source, tourmaline (6). The boron equilibrium appeared to have shifted with seasonal conditions, however, for the value was only 0.14 ppm. when the experiment was begun in April, but rose to 0.17 ppm. through the hot, wet summer months, and dropped with lower temperature and scarcity of moisture to 0.12 ppm. in October. The cyclic period of maximum liberation appears to have been reached again by May 17 of the following year, when the boiling-water-extractable boron rose to 0.18 ppm.

Data from the detailed study of the influence of cultivation and seasonal change in the various soil types are presented in table 2. Location 34 showed an extreme response of a virgin soil to seasonal variation, with respective boron values for winter dry, summer dry, and summer wet of 0.18, 0.33, and 0.52 ppm.

TABLE 1

Boiling-water-extractable boron in Arredondo loamy fine sand (shallow phase) as related to sampling period, temperature, and rainfall

DATE SAMPLED	BORON 0-7 INCH DEPTH	MEAN TEMPERATURE	RAINFALL		
			3 days prior to sampling	Since previous sampling period	Total since Apr. 20
	ppm.	°F.	in.	in.	in.
(1945) *Apr. 20	0.14	73.8	0.12	*	—
June 26	0.17	81.6	2.63	11.67	11.67
July 20	0.17	80.4	2.75	7.84	19.51
Aug. 21	0.17	80.6	5.52	14.24	33.75
Sept. 18	0.17	80.4	1.59	6.74	40.49
Oct. 22	0.12	71.6	0.00	0.75	41.24
(1946) May 17	0.18	76.2	0.77	25.14	66.38

* The rainfall in April prior to the first sampling was 0.35 inch (0.23 for April 7 and 0.12 for April 19).

In location 36, companion to 34 except cultivated for about 50 years, there was an almost parallel response to seasonal change, with respective boron values of 0.06, 0.14, and 0.16 ppm. There was a similar response to climate in all soils to and including location 97. In location 106, where the soil was protected by trees, shrubs, and the A₀ organic mat, there was the usual seasonal gain in boron, with values of 0.13, 0.19, and 0.25 ppm. In the adjoining peanut field (location 107), which had been under cultivation for about 75 years, the winter dry value was only 0.05 ppm. This rose to 0.09 ppm. for the summer dry period, but in the August sampling² dropped to 0.07 ppm.

In the lower section of table 2 the increase in summer dry (June) values over winter wet was notable in all instances, with gains of 116 to 550 per cent. As in location 107, however, there was a loss of boron in the August samples; yet these still exceeded the winter wet by 42 to 250 per cent. August losses from the deep

² See footnote, table 2.

sandy soils should be contrasted with excellent retention by the soil in table 1, where depth to clay was limited. From the means for the upper section of table 2 it is seen that climatic effects in the virgin soils caused boron to rise from 0.22 ppm. for winter dry to 0.38 ppm. for summer wet, and in the cultivated soils from 0.07 ppm. to 0.19 ppm. Therefore, the virgin soils showed a seasonal gain in boron of 73 per cent, and the corresponding gain in cultivated soils was 171 per cent.

TABLE 2

Variation in boiling-water-extractable boron with prolonged cultivation and seasonal change
Expressed as parts of boron per million parts of air-dried soil

LOCATION NUMBERS VIRGIN; CULTIVATED	SOIL TYPE	VIRGIN			CULTIVATED		
		Winter dry (January)	Summer dry (June)	Summer wet (August)	Winter dry (January)	Summer dry (June)	Summer wet (August)
34; 36	Blichton fine sand	0.18	0.33	0.52	0.06	0.14	0.16
49; 50	Blichton loamy fine sand	0.28	0.35	0.45	0.14	0.24	0.32
51; 52	Arredondo loamy fine sand	0.23	0.35	0.41	0.08	0.23	0.25
83; 84	Blichton loamy fine sand	0.33	0.35	0.38	0.03	0.10	0.14
96; 97	Kanapaha fine sand	0.17	0.22	0.28	0.04	0.14	0.20
106; 107	Blanton fine sand	0.13	0.19	0.25*	0.05	0.09	0.07*
Mean		0.22	0.30	0.38	0.07	0.16	0.19
		Winter wet (February)	Summer dry (June)	Summer wet (August)	Winter wet (February)	Summer dry (June)	Summer wet (August)
121; 122	Ft. Meade fine sand	0.19	0.41	0.27*	0.09	0.30	0.13*
123; 124	Gainesville loamy fine sand	0.15	0.34	0.23*	0.06	0.23	0.12*
127; 128	Jonesville fine sand	0.04	0.17	0.09*	0.02	0.13	0.07*
Mean		0.13	0.31	0.20	0.06	0.22	0.11

* From sections of the county where summer rains were late. There had been only one major rainy period, of 24 to 48 hours' duration, and ending 3 days before these samples were taken. Leaching of boron appears to have been heavy in most instances, with insufficient time for reestablishment of equilibrium before the samples were taken.

The total amount of boiling-water-extractable boron found in the cultivated soils was notably less than in the virgin soils. This relationship is given in detail in table 3. Though the ratios are somewhat variable, the boron in cultivated soils never exceeded 78 per cent of the amount found in the corresponding virgin soil. In location 84, where the soil had been under cultivation for about 100 years, the cultivated field showed only 9 per cent as much boron as the adjoining hardwood forest. But this low value was for the conditions of the January sampling. When sampled in June (dry) the cultivated soil showed 29 per cent as much boron as the virgin sample, and in August (consistently wet) 37 per cent as much. The mean values for table 3 show that when sampled in winter the boron in culti-

vated soils was only 36 per cent of that in the virgin soils, but rose to 59 per cent in the June samples, and was 53 per cent of the virgin values in the samples collected in August.

Limited data were obtained as to management practices which might have a tendency to restore boiling-water-extractable boron in cultivated soils to the original virgin levels. In two areas it was possible to collect samples not only from virgin and cultivated locations but also from locations where the soil had been allowed to revert to a growth of volunteer pines in the first instance and to weeds and bushes in the second. As all these samples were collected at the same

TABLE 3

Ratio of boiling-water-extractable boron in cultivated soils to that in corresponding virgin soils under various climatic conditions

Value for virgin soil in each instance considered as 1.00

LOCATION NUMBERS	SOIL TYPE	WINTER (JANUARY-FEBRUARY)	SUMMER DRY (JUNE)	SUMMER WET (AUGUST)
34; 36	Blichton fine sand	0.33	0.42	0.31
49; 50	Blichton loamy fine sand	0.50	0.69	0.71
51; 52	Arredondo loamy fine sand	0.35	0.66	0.61
83; 84	Blichton loamy fine sand	0.09	0.29	0.37
96; 97	Kanapaha fine sand	0.24	0.64	0.71
106; 107	Blanton fine sand	0.38	0.47	0.28
121; 122*	Ft. Meade fine sand	0.47	0.73	0.48
123; 124	Gainesville loamy fine sand	0.40	0.68	0.52
127; 128	Jonesville fine sand	0.50	0.76	0.78
Mean		0.36	0.59	0.53

* The break used in table 2 to set off locations 121 to 128 has been eliminated here, as the rain 2 days prior to the February sampling seems to have caused little difference in the ratios for these soils.

time, they are validly comparable one with another. The analytical values as parts per million are as follows:

Locations	Virgin	Cultivated	Reverted
34;36;35 Blichton fine sand.....	0.18	0.06	0.10
31;33;32 Gainesville loamy fine sand.....	0.23	0.11	0.14

Location 36, under long cultivation, contained 0.06 ppm. compared with the virgin value of 0.18 ppm., but after reversion to pines (location 35) the value had risen to 0.10 ppm. This gain of 0.04 ppm. indicates a 33 per cent restoration of soluble boron in about a 12- to 15-year period. In the second group the gain of 0.03 ppm. for location 32 represents a 25 per cent restoration in what seemed to have been less than a 10-year period.

DISCUSSION

Analytical procedures for soil boron are now relatively satisfactory, but wide sampling variations due to seasonal effects may lead to erroneous conclusions.

Such variations appear to result from shifts in the equilibrium between the primary source of boron, tourmaline, and the natural soil processes. Types of investigation in which this phenomenon could cause major errors are: a study of the effects of various soil amendments upon boron levels in soils; a study of residual effects of boron supplements; and a survey to establish critical levels for boron in soils, relative to plant response.

Since it has been shown by various investigators that boron uptake by plants is very limited in times of drought, it might be assumed that there is some type of fixation in a dry soil. The data presented herein have shown a considerable gain in water-extractable boron in soils sampled in an extremely dry time but at elevated temperatures. It is concluded for certain sandy soils during periods of summer drought, therefore, that the movement of boron from soil to plant is limited primarily by the lack of water as a transporting vehicle.

SUMMARY

Upland mineral soils in Alachua County, Florida, were sampled in January, June, and August, to study variations in the boiling-water-extractable boron in virgin and cultivated soils under the following seasonal conditions: winter dry, summer dry, and summer wet. In Blichton fine sand the boron for these respective periods was 0.18, 0.33, and 0.52 ppm. for the virgin samples, and 0.06, 0.14, and 0.16 ppm. for the cultivated. The other soil types showed similar climatic response. Blanton fine sand under native cover contained 0.13, 0.19, and 0.25 ppm., respectively; but in the adjoining peanut field cultivated 75 years, the winter dry value was only 0.05 ppm. This rose to 0.09 ppm. under hot, dry June conditions, but decreased to 0.07 ppm. where the August rains were intense but occurred only 3 days prior to sampling.

In Blichton loamy fine sand cultivated approximately 100 years the January samples showed only 9 per cent as much boiling-water-extractable boron in the cultivated field as in the adjoining virgin area (hardwood forest). In the June (dry) samples the boron value increased to 29 per cent as much as in the virgin soil and in the August (consistently wet) samples to 37 per cent as much.

The need for evaluation of seasonal conditions in sampling soils for the boron determination is emphasized.

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EFFECT OF SULFUR FERTILIZATION ON THE VITAMIN CONTENT OF ALFALFA

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Received for publication January 14, 1952

Sulfur occurs in plants and animals both as inorganic sulfate and as a constituent of organic compounds. It is present in the amino acids methionine and cystine, in the vitamins thiamine and biotin, in the peptide glutathione, and in a number of other compounds which are important in the general metabolism of plants and animals.

The level of sulfur fertility of the soil directly affects the total sulfur of the plant (11, 15, 21). Thomas *et al.* (19) reported a twelvefold range in the total sulfur content of alfalfa leaves, depending on the sulfur supply to the plants. These variations were due mainly to the inorganic fraction. It has been established that a sulfur deficiency in soils lowers the crop yield (5). This indicates that the general metabolism of the plant has been modified and that substances other than those containing sulfur are affected.

Tisdale *et al.* (20) found that methionine and cystine decreased in alfalfa which was grown in nutrient solutions deficient in sulfate but were not increased above normal by an excess of sulfate. Recently, Mertz *et al.* (12) found that sulfur-deficient alfalfa plants grown in sand culture contained increased amounts of aspartic acid and arginine and decreased amounts of 16 other amino acids when compared with normal control alfalfa plants. The samples used in this latter experiment were also analyzed for the B vitamins, and the results of these assays are reported in this paper.

Little work has been published on the relation of sulfur fertility to the vitamin content of plants. It has been reported (7, 10) that the carotene and ascorbic acid contents of ripe tomatoes were not significantly influenced by wide variations in the sulfate supplied to the plant. In complete absence of sulfate, however, the ascorbic acid content was slightly higher than average. Essentially the same results were observed on the carotene and ascorbic acid contents of turnip greens (2). When the turnips were grown either in soil or in sand cultures, the ascorbic acid content was affected little by the sulfate supply; however, deficiencies in sulfate caused a decrease in the carotene content of the turnip greens when in sand cultures, but not in soil. Any treatment that produced visible chlorosis of the leaves resulted in appreciable decreases in the carotene content.

Reports on the effect of sulfur fertility on the B-vitamin content of plants have been limited to the studies by Watson and Noggle (22), who found somewhat lower riboflavin values for sulfur-deficient oat plants grown on gravel culture than for those grown with complete nutrient solutions. The present work

¹ Journal Paper 595, Purdue University Agricultural Experiment Station, Lafayette, Indiana. This work was supported in part by the Texas Gulf Sulphur Company.

was conducted to determine the effect of sulfur treatments upon the vitamin B-complex of alfalfa.

MATERIALS AND METHODS

Plants were grown on soil plots with varying applications of elemental sulfur to the soil, as well as in sand culture pots in the greenhouse. The entire plants except the roots were analyzed for seven of the water-soluble vitamins: biotin, folic acid, niacin, pantothenic acid, pyridoxine, riboflavin, and thiamine. Choline was also determined in some samples. In addition, amounts of total, inorganic, and organic sulfur were determined in order to correlate sulfur treatment with the sulfur and vitamin content of the plant material.

Alfalfa grown in field plots

Samples were taken from alfalfa plants grown in Culver fine sand near Culver, Indiana, in a randomized block design which received five treatments in three replications by adding elemental sulfur at the rate of 112, 224, 448, and 896 pounds per acre. Three cuttings were harvested in 1949. Since there was no difference in yield between treatments in any of the cuttings, only the extreme levels were analyzed for vitamin content, that is, the control plots and those treated with 896 pounds of sulfur per acre.

The alfalfa samples were dried at 60°C. for 24 hours in an oven equipped with a blower, ground in a Wiley mill to pass a 0.5-mm. sieve, mixed, bottled, and stored at -18°C.

Alfalfa grown in nutrient solution

Samples were taken from alfalfa plants grown in the greenhouse in sand culture according to a procedure described by Tisdale *et al.* (20). All of the plants were propagated from the same clone and hence were genetically identical. The cuttings were rooted in a medium of quartz sand and vermiculite with the aid of indolbutyric acid, given one application of a complete nutrient solution and kept moist with distilled water until vigorous root systems had formed, and then transplanted in the test pots containing washed flint-shot quartz sand. One series of six pots was treated with the complete nutrient solution in which the SO_4 -ion concentration was 81 ppm.; the other series of 14 pots was treated with a similar nutrient solution except that it contained no SO_4 ions. The only source of sulfur for the negative pots was from the atmosphere (9), which was apparently inadequate. Three cuttings of the plant materials were harvested, dried in an air oven at 65°C. for 10-12 hours, ground in a Wiley mill to pass a 0.5-mm. sieve, weighed, and composite samples made of the material from the pots of each treatment.

Methods of analysis

Moisture was determined by drying the samples at 70°C. for 5 hours at reduced pressure in a vacuum oven. Total sulfur was determined by the combustion method with a Parr oxygen bomb (14, p. 40). The dry plant material

(1.4–1.8 gm.) was compressed into a hard pellet with the pellet-maker supplied with the apparatus, weighed accurately, and subjected to combustion in the bomb. The sulfate was precipitated from an acid solution of the residue with 1 per cent solution of BaCl_2 . From the weight of BaSO_4 the percentage of sulfate was calculated on a dry-weight basis.

Sulfate sulfur was determined according to the following procedure:

A 5.000-gm. sample of dry plant material was extracted with 30 ml. of distilled water for about an hour with occasional shaking. The supernatant solution was filtered through a Whatman No. 2 paper. The residue was washed four times, after which it was transferred to the filter and washed with distilled water until a total volume of about 200 ml. was obtained. The extract was treated with 2 ml. of bromine water, evaporated to dryness on the steam bath, and then charred in a muffle furnace at 600° for 5 minutes. After cooling, 15 ml. of water and 0.5 ml. of concentrated HCl were added, the solution was filtered through Whatman No. 2 paper, and the filter washed with hot distilled water until the volume was about 150 ml. The sulfate was precipitated as BaSO_4 . Results are expressed as percentage of sulfur on a dry-weight basis. Organic sulfur was calculated from the difference between total sulfur and sulfate sulfur.

Thiamine was determined by the thiochrome method (1), except for minor modifications as suggested by Brown *et al.* (4). Choline was determined by the method of Engel (8). The other vitamins were determined microbiologically. Biotin was assayed by the procedure of Wright and Skeggs (23); niacin and riboflavin by the procedures outlined in *Methods of Vitamin Assay* (1); pyridoxine by the method of Stokes *et al.* (17); and pantothenic acid according to Skeggs and Wright (16) after enzymatic release of the vitamin (13). Folic acid in the samples from the field plots was assayed with *Lactobacillus casei* (18), and the samples from the pot culture series were assayed with *Streptococcus faecalis R* (6, pp. 159–160). Although a comparison of the two methods on the same sample indicated that *S. faecalis* gave slightly higher values than *L. casei*, the values within each series are comparable.

RESULTS AND DISCUSSION

The sulfur and vitamin contents of the alfalfa grown in the field plots are given in table 1. There was little difference between the vitamin contents or sulfur contents of the plants grown on plots without added sulfur and those grown with an excess of sulfur. On subjecting the data to analyses of variance, it was found that the differences resulting from sulfur treatment were not significant at the 5 per cent level, although the differences between cuttings were significant. The first cutting appeared to have the highest vitamin content; the second cutting was lower than the first and third except for folic acid and biotin.

The lack of significant differences between treatments suggests that the soils contained an adequate amount of sulfur for normal growth as evidenced by lack of yield differences and visible deficiency symptoms, and that an application of excess sulfur to the soil did not increase the vitamin content of the plants.

Since Bertamson *et al.* (3) have reported that sulfur deficiency probably does not exist in most parts of Indiana, and since no chlorosis or decreased yields were

noted in the alfalfa from the untreated plants, a deficiency of sulfur probably did not exist.

It was surprising that the application of large amounts of sulfur had no marked effect on the sulfur fractions of plants, since various investigators have shown that increased sulfur supply produced increased amounts of total sulfur, regardless of the needs of the plant. Although no climatological data were recorded, the amounts of sulfur from rainfall (3) during the growth of the plants may have been partly responsible for the results obtained in this experiment.

TABLE 1
Vitamin and sulfur content of alfalfa grown on soil treated with sulfur, 1949 series

	TREAT- MENT, ELEMEN- TAL SUL- FUR PER ACRE	SULFUR		VITAMIN* PER GRAM DRY WEIGHT							
		Total	Or- ganic	Biotin	Cho- line	Folic acid	Niacin	Panto- thenic acid	Pyri- doxine	Ribo- flavin	Thia- mine
	lb.	%	%	γ	γ	γ	γ	γ	γ	γ	γ
First cutting	0	0.294	0.18	0.46	2,100	2.3	43	32	8.0	12	5.7
	896	0.327	0.20	0.57	1,800	3.1	44	37	7.0	10	5.9
Second cutting	0	0.260	0.15	0.48	900	3.1	32	21	5.2	8.4	5.5
	896	0.275	0.15	0.51	930	3.6	32	21	5.2	7.0	5.4
Third cutting	0	0.304	0.18	0.50	1,300	2.4	35	51	6.7	8.3	4.8
	896	0.309	0.19	0.41	1,600	2.3	36	46	6.6	7.1	5.0
Average for cuttings											
1		0.311	0.20	0.51	1,900	2.7	43	35	7.5	11.0	5.8
2		0.268	0.15	0.49	910	3.3	32	21	5.2	7.7	5.4
3		0.307	0.18	0.45	1,400	2.3	35	48	6.6	8.1	5.8
LSD (5%)		0.015	0.01	0.10	440	0.6	3.6	5.3	0.7	0.9	0.2
LSD (1%)		0.021	0.02	0.15	640	0.9	5.2	7.8	1.0	1.1	0.4
Average for treatments	0	0.286	0.17	0.48	1,400	2.6	37.0	35	6.6	9.5	5.3
	896	0.304	0.18	0.50	1,400	3.0	37.0	35	6.3	8.2	5.4
LSD (5%)		0.038	0.02	0.10	600	0.9	3.5	6.1	0.5	2.9	0.3

* Each entry is the average of one determination on each of three replicates.

In an attempt to produce sulfur-deficient plants, oats and alfalfa were grown in soil pots in the greenhouse. Elemental sulfur at the rate of 1,600 pounds per acre was added to one series of pots and no sulfur to the control pots. Because of lack of chlorosis, and no differences in yields and vitamin contents, these results are not reported.

Changes due to sulfur deficiency were not produced until alfalfa plants were grown in sand culture under rigorously controlled conditions. During growth of the first cutting there was little apparent difference in the plants grown without

and with addition of 81 ppm. of sulfate, probably because of the sulfur present in the cuttings or because of some sulfur taken up by the plants during the process of rooting in the complete nutrient solution. No deficiency symptoms were apparent in the deficient plants at the time of the first cutting. When the second cutting was made, however, the plants in the deficient pots were stunted and yellow. At the time of the third cutting, the plants had made very little growth, the leaves were chlorotic, and the stems were spindly. The yields were reduced to 97 per cent of the controls in the first cutting, 38 per cent in the second, and 16 per cent in the third.

The sulfur and vitamin contents of these samples are given in table 2. Although 14 pots were used to grow the sulfur-deficient plants, the yields were so small that it was necessary to make composite samples of each cutting for analysis.

TABLE 2

Vitamin and sulfur content of alfalfa grown in nutrient solution with and without sulfate

CUTTING	SULFATE TREATMENT IN NU- TRIENT SOLUTION	SULFUR			VITAMIN (PER GRAM DRY WEIGHT)						
		Total	Sulfate	Or- ganic	Biotin	Folic acid	Niacin	Panto- thenic acid	Pyri- doxine	Ribo- flavin	Thia- mine
	ppm.	%	%	%	γ	γ	γ	γ	γ	γ	γ
First	81	0.356	0.22	0.14	0.52	6.0	41	61	9.0	13	6.3
	0	0.234	0.13	0.10	0.45	5.0	37	55	7.8	11	5.8
		[66]*	[55]	[71]	[87]	[83]	[90]	[90]	[87]	[85]	[92]
Second	81	0.341	0.19	0.15	0.58	5.8	46	62	11	16	6.2
	0	0.119	0.03	0.09	0.24	3.0	42	49	7.4	10	4.6
		[32]	[15]	[60]	[41]	[52]	[91]	[79]	[63]	[63]	[74]
Third	81	0.350	0.20	0.15	0.51	5.0	39	60	12	18	6.0
	0	0.080	0.03	0.05	0.22	1.0	41	25	6.5	8.9	3.4
		[23]	[17]	[33]	[43]	[20]	[105]	[42]	[54]	[49]	[57]

* Figures in brackets are percentages of the amounts in the material grown in complete nutrient solution.

Consequently, the data could not be analyzed for significance. When compared with the control plants, the deficient plants of each cutting showed a progressive decrease in the sulfur content and all the vitamins except niacin. The magnitude of the differences, especially in the third cutting, appear to warrant the conclusion that when sulfur deficiency is sufficiently severe to affect the growth and produce chlorosis in the plant, a definite decrease of the total sulfur, the organic sulfur, and many of the vitamins occurs. The tests indicate that when the organic sulfur content of the plants is reduced to 0.10 per cent or less, definite symptoms of chlorosis appear, whereas at levels above 0.15 per cent (table 1) no chlorosis or reduced yields were produced. At levels of 0.10 per cent or less of organic sulfur, visible chlorosis and decreased B-vitamin content resulted.

It was observed that the sulfur-containing vitamins, thiamin and biotin, were affected no more severely by sulfur deficiency than were many of the other vita-

mins. Mertz *et al.* (12) found that the sulfur-containing amino acids of these same samples were decreased no more than were many of the other amino acids. This would indicate that sulfur deficiency affects the general metabolism, which in turn affects a number of constituents, among which are the vitamins and amino acids.

SUMMARY

To determine the effect of sulfur deficiency and sulfur fertilization on the vitamin-B content of alfalfa, plants were grown in field plots and in nutrient culture in the greenhouse with and without additions of sulfur and were analyzed for biotin, choline, folic acid, niacin, pantothenic acid, pyridoxine, riboflavin, thiamine, and inorganic, organic, and total sulfur.

Alfalfa grown on soil treated with 896 pounds of sulfur per acre failed to show any significant increase in the vitamin or sulfur content over that grown on soil which received no sulfur treatment.

To obtain sulfur-deficient plants, it was necessary to use sand culture technique. Plants grown with sulfur-deficient nutrient solution contained much smaller amounts of six of the B vitamins than did those grown in complete nutrient solution (81 ppm. sulfate). The content of niacin was not affected. The sulfur-deficient plants of the third cutting contained one fifth as much folic acid and about one half as much biotin, pantothenic acid, pyridoxine, riboflavin, and thiamine as did the control plants. The sulfur-containing vitamins, biotin and thiamine were affected no more than some of the other vitamins, although the total, inorganic, and organic sulfur contents were greatly reduced in the sulfur-deficient plants.

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UTILIZATION OF PHOSPHORUS FROM BARLEY RESIDUES

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Received for publication January 17, 1952

Barley is one of the leading winter crops in the irrigated valleys of Arizona, and every year considerable quantities of the straw and roots are tilled into the soils. The plant nutrients in these residues are not insignificant. The phosphorous content, for example, is usually 0.2 to 0.5 per cent on a dry-weight basis. Such mineral elements eventually contribute to succeeding crops as a result of microbial decomposition, a process that ultimately releases organically combined elements for plant absorption. Except for the recent investigations of Fuller and Dean (4) with soybean and wheat straw and a limited study by White *et al.* (9) with alfalfa, little is known about the rate and extent of phosphorus uptake from plant residues by succeeding crops. That such information is limited is indicated also by the very few soils represented in these studies. Calcareous soils of the irrigated valleys in the western states, for example, were not included in the investigations.

The ready availability of radioisotopes in recent years has permitted expansion of research work involving the identification of single elements from two or more separate sources. By "tagging" the phosphorus in plant residues placed in soils, for example, one can distinguish the amount of the element taken up from the residue and from the soil by a newly planted crop.

The greenhouse investigations reported here were conducted to obtain information about the utilization of phosphorus by rye grass from barley materials at three stages of maturity as compared with liquid phosphoric acid when incorporated in some calcareous semiarid soils.

MATERIALS AND METHODS

Labeled barley materials

Barley materials containing radiophosphorus were prepared by growing Arivat barley in steel flats (48 by 24 by 6 inches) containing Ottawa silica sand and subirrigated daily with a balanced nutrient solution except for phosphorus, which was omitted during the early stages of growth. The same procedure and the same concentration of P32 used for the preparation of labeled wheat by Fuller and Dean (4) were used in this investigation. Barley harvests were made after 32, 52, and 95 days of growth and yielded young barley hay, medium mature barley hay, and mature straw. Tops and roots were harvested separately. Plant materials were washed in water to remove chance contamination by radiophosphorus from outside sources. Barley heads were clipped from the mature plants

¹ Cooperative project between the University of Arizona and the Biology Branch, Division of Biology and Medicine, Atomic Energy Commission under contract No. AT (11-1)-103.

and the seeds removed. Hulls from unfertilized seeds were separated from the grain. Table 1 shows the composition of the barley.

Soils

Soils employed in this investigation were selected for their agricultural importance as well as their wide variation in organic matter, CO₂-soluble phosphorus, and CaCO₃ content. Table 2 shows the chemical characteristics of the six soils used.

TABLE 1
Composition of barley materials added to soils

PLANT MATERIAL	AGE	CARBON	NITROGEN	TOTAL PHOSPHORUS	ORGANIC PHOSPHORUS
	<i>days</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Young hay.....	32	34.8	5.46	0.287	0.065
Medium mature hay.....	52	33.6	2.10	0.352	0.072
Mature straw*.....	95	34.5	1.98	0.225	0.040
Roots of medium mature hay.....	52	34.9	0.94	0.159	0.044
Roots of mature straw*.....	95	30.9	1.11	0.239	0.064
Grain.....	95	40.5	4.25	0.567	0.480
Hulls unfertilized.....	95	38.1	1.47	0.467	0.078
Chaff and awns.....	95	29.4	1.35	0.383	0.133

* Grain heads removed at maturity.

TABLE 2
Chemical analysis of soils used in the greenhouse experiment

SOIL TYPE	LAND USE	DEPTH	pH	N	PHOSPHORUS			C	C/N RATIO	CaCO ₃
					Total	Or- ganic	CO ₂ - Soluble			
		<i>in.</i>		<i>per cent</i>	<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>	<i>per cent</i>		<i>per cent</i>
Pima clay loam.....	Virgin	0-6	8.1	0.228	1580	760	13.00	2.50	11.0	0.2
McClellan clay loam.....	Virgin	0-6	8.1	0.090	995	279	1.44	0.74	8.2	6.3
McClellan clay loam.....	Cultivated	0-6	8.0	0.058	390	85	0.70	0.46	8.0	0.4
Mohave clay loam.....	Cultivated	0-6	8.2	0.053	515	108	1.24	0.45	8.6	1.5
Mohave clay loam.....	Cultivated	6-12	8.2	0.029	495	89	0.82	0.26	9.0	1.5
Verde fine sandy loam.....	Cultivated	0-6	8.0	0.087	1020	130	0.80	0.75	8.7	12.5

Chemical analysis

Chemical analyses of the barley materials and soils, shown in tables 1 and 2, respectively, were made according to the following methods:

Plant analysis. Nitrogen was determined by the Kjeldahl method, carbon by dry combustion, and phosphorus by the molybdivanado-phosphoric acid method (5). Organic phosphorus was determined by the method of Pons and Guthrie (8) slightly modified. Refrigerated trichloroacetic acid was used to keep the temperature below 10° C. during the phosphorus extraction.

Soils. Nitrogen was determined by the Kjeldahl method, carbon by wet oxidation (1), total phosphorus by the standard NaCO_3 fusion followed by the colorimetric procedure of Dickman and Bray (3), and organic phosphorus by Pearson's (7) method.

Measurement of P31 and P32. The method of MacKenzie and Dean (6) was used.

Greenhouse pot experiment

Half-gallon glazed pots, each containing 1 kgm. of soil, were set up in the greenhouse and treated in triplicate with plant material and liquid phosphoric acid at the rate of 46 pounds P_2O_5 per acre. This amounted to 3.48 tons young hay, 2.84 tons medium mature hay, 4.44 tons mature straw, 6.29 tons medium mature roots, 5.94 tons mature roots, 1.76 tons grain flour, 2.14 tons hulls, and 2.61 tons chaff per acre-6-inch layer. All treatments were made in a layer 3 inches below the surface. The barley hay and straw materials were chopped into pieces $\frac{1}{2}$ inch long before application. Radioactive liquid H_3PO_4 was prepared by adding radioactive KH_2PO_4 to a known amount of H_3PO_4 to give a specific activity similar to that of the phosphorus of barley straw.

After incubation for 7 days in a damp condition, the pots were seeded to perennial rye grass. Cuttings were made 6 weeks after planting. Further cuttings were made at intervals of 4 weeks.

RESULTS

Phosphorus uptake as function of source of material

That stage of maturity was an important factor influencing the utilization of phosphorus of barley straw by rye grass is shown clearly in table 3. The difference in utilization between the young and the medium mature barley hay appeared to be less than that between the medium mature hay and the mature straw. It was at first speculated that differences in utilization reflected differences in the nature of the phosphorus compounds in the straws. Analysis of the straws according to the Pons and Guthrie method, however, showed that the ratio of organic to inorganic phosphorus was not greatly influenced by stage of maturity. Percentages of inorganic phosphorus, for example, were found to be 76.7, 79.5, and 82.2 for the young hay, medium mature hay, and mature straw, respectively. The difference between these figures and 100 is considered to be percentage of organic phosphorus.

In general, utilization of the phosphorus of the barley roots by the rye grass was less than that of the corresponding straw. The order of decreasing uptake of phosphorus from the different parts of *mature* barley was found to be chaff and awns, hulls, straw, flour = roots. Percentages of inorganic phosphorus for these materials in the same order are 65.3, 83.4, 82.2, 15.3, and **73.2**.

The phosphorus of the liquid phosphoric acid added to the soils, on a phosphorus basis equivalent to the plant materials, appeared to be no more available to rye grass than did that of the young barley hay, medium hay, chaff and awns, and hulls.

TABLE 3

Yield, phosphorus content of rye grass, and percentage phosphorus in rye grass derived from various barley materials and liquid H_3PO_4 in six soils

TREATMENT	DRY WEIGHT PER POT			P IN GRASS			P IN GRASS FROM TREATMENT		
	Cut- ting 1	Cut- ting 2	Cut- ting 3	Cut- ting 1	Cut- ting 2	Cut- ting 3	Cut- ting 1	Cut- ting 2	Cut- ting 3
	gm.	gm.	gm.	%	%	%	%	%	%
<i>McClellan clay loam (virgin)</i>									
Young hay.....	7.20	3.24	3.95	0.138	0.138	0.140	36.1	36.1	36.2
Medium hay.....	2.90	2.28	3.68	0.260	0.218	0.130	33.6	33.0	31.7
Mature straw.....	2.37	2.05		0.276	0.220		25.4	26.9	
Roots of medium hay.....	1.84	1.44	3.58	0.270	0.251	0.151	23.4	25.9	25.3
Roots of mature straw.....	1.66	1.04		0.169	0.265		25.9	25.1	
Grain flour.....	2.44	2.13	1.87	0.293	0.228	0.193	23.1	23.6	23.4
Hulls.....	2.82	1.73		0.278	0.292		37.5	37.8	
Chaff and awns.....	3.35	1.79		0.245	0.310		40.2	40.5	
Liquid H_3PO_4	2.48	1.44	3.34	0.323	0.200	0.126	38.4	35.0	30.3
None.....	2.36	1.40	2.58	0.188	0.182	0.135			
<i>McClellan clay loam (cultivated)</i>									
Young hay.....	3.43	2.89	3.91	0.133	0.125	0.112	54.1	54.1	54.9
Medium hay.....	1.82	1.46	3.82	0.249	0.239	0.104	48.3	49.3	42.8
Mature straw.....	2.12	1.77		0.205	0.189		41.6	40.1	
Roots of medium hay.....	1.26	1.00	3.02	0.266	0.240	0.088	35.5	29.1	36.6
Roots of mature straw.....	0.74	1.10		0.329	0.184		33.5	24.3	
Grain flour.....	2.94	2.80		0.124	0.136		29.6	31.9	
Hulls.....	1.97	1.48		0.257	0.227		41.9	48.9	
Chaff and Awns.....	2.12	1.15		0.204	0.254		53.8	68.4	
Liquid H_3PO_4	1.12	0.90	3.20	0.320	0.228	0.119	49.2	54.8	51.0
None.....	1.24	0.86	1.14	0.098	0.086	0.061			
<i>Pima clay loam (virgin)</i>									
Young hay.....	11.46	9.21		0.281	0.261		16.1	16.3	
Mature straw.....	6.82	6.64		0.253	0.219		10.7	14.7	
Roots of mature straw.....	6.40	6.32		0.209	0.181		5.6	10.7	
Grain flour.....	8.26	6.20		0.229	0.215		6.0	6.8	
Hulls.....	8.36	4.84		0.338	0.264		16.3	16.4	
Chaff and awns.....	8.68	4.49		0.270	0.266		24.2	20.0	
Liquid H_3PO_4	8.02	5.80		0.334	0.246		20.5	15.0	
None.....	7.32	5.92		0.298	0.201				
<i>Verde fine sandy loam (cultivated)</i>									
Mature straw.....	2.92	2.04		0.118	0.106		29.3	29.8	
Hulls.....	2.34	1.62		0.157	0.235		48.8	36.8	
Chaff and awns.....	2.18	1.24		0.178	0.286		54.1	38.4	
Liquid H_3PO_4	2.32	1.38		0.166	0.226		36.5	28.2	
None.....	1.68	1.34		0.083	0.108				

TABLE 3—Continued

TREATMENT	DRY WEIGHT PER POT			P IN GRASS			P IN GRASS FROM TREATMENT		
	Cut- ting 1	Cut- ting 2	Cut- ting 3	Cut- ting 1	Cut- ting 2	Cut- ting 3	Cut- ting 1	Cut- ting 2	Cut- ting 3
	gm.	gm.	gm.	%	%	%	%	%	%
<i>Mohave clay loam (cultivated), 0-6 inches</i>									
Mature straw	2.68	1.46		0.231	0.177		20.6	17.5	
Hulls	2.90	1.48		0.225	0.242		35.9	27.9	
Chaff and awns	2.78	1.62		0.222	0.257		37.9	31.3	
Liquid H ₃ PO ₄	2.70	1.18		0.227	0.251		30.9	23.9	
None	2.08	1.22		0.129	0.151				
<i>Mohave (cultivated), 6-12 inches</i>									
Mature straw	2.72	0.88		0.209	0.278		21.0	21.2	
Hulls	1.86	0.98		0.237	0.361		37.8	30.7	
Chaff and awns	1.72	0.68		0.211	0.382		44.1	35.0	
Liquid H ₃ PO ₄	2.16	0.84		0.241	0.345		30.0	25.3	
None	1.96	0.68		0.102	0.111				

Phosphorus utilization in different soils

The percentage of phosphorus in the rye grass taken from the plant materials and liquid phosphoric acid was greatest from those soils least well supplied with CO₂-soluble phosphorus. Pima clay loam was the only soil unquestionably not deficient in "available" phosphorus according to the CO₂-method. Utilization of added phosphorus sources was decidedly less in this than in the other soils. The virgin McClellan clay loam was better supplied with CO₂-soluble phosphorus than the same soil under cultivation. Data in table 3 reflect this difference in fertility level, for the grass on the cultivated soil utilized the added phosphorus more extensively than did that grown on the virgin soil. The grass on the other phosphorus-"poor" soils also took a larger proportion of its phosphorus from the added residues than did that on the virgin soils. There was little difference in uptake between the 0-6 and 6-12-inch layers of Mohave clay loam. This was to be expected, since the layers differed little in their chemical and physical characteristics.

Yields and percentage phosphorus in grass

The nature of the plant residue incorporated into the soil influenced the yield of grass grown on the soil as well as the percentage total phosphorus found in the grass (table 3). Soils treated with young barley hay, for example, produced much more grass than did those treated with the other residues. Moreover, the percentage phosphorus in this grass, more often than not, was lower than that harvested from soils treated with mature barley materials. Barley roots from two sources, on the other hand, depressed grass yields in many instances below that of soil

alone, though the percentage phosphorus of the grass was higher than that of the untreated soils. The grass from the six soils treated with the liquid H_3PO_4 had a higher mean phosphorus content than did that of all the other treatments at the time of the first cutting. This was not the case for the grass of the second and third cuttings. Grass yields were only slightly improved by application of liquid H_3PO_4 over those of soil alone.

Because of low yields and indications of nitrogen deficiency both the virgin and cultivated McClellan soils treated with medium mature hay, roots, and liquid H_3PO_4 were given applications of urea equivalent to 100 pounds of N per acre after the second cutting of rye grass. The data in table 3 show that the third-

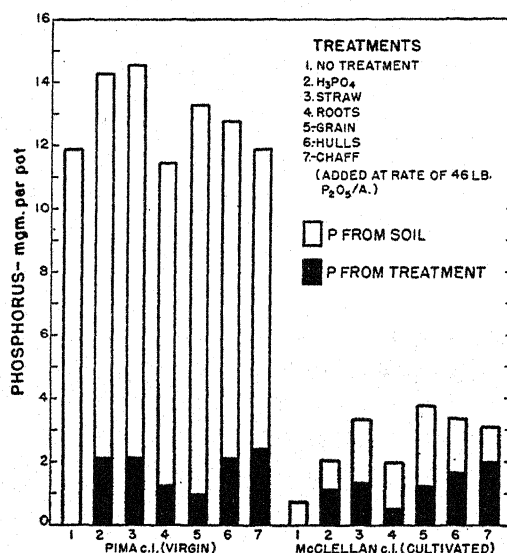


FIG. 1. TOTAL PHOSPHORUS UPTAKE FROM DIFFERENT PARTS OF MATURE BARLEY PLANTS BY RYE GRASS IN TOL SOILS AS COMPARED WITH THE UPTAKE FROM LIQUID H_3PO_4

cutting rye grass yields were markedly increased by the nitrogen application, though the phosphorus, on a percentage dry weight basis, was only slightly lower than in previous cuttings. Calculations of total phosphorus show that nitrogen increased absolute uptake over that of the first and second cuttings. The proportion of phosphorus taken from the soil and the added sources, however, remained the same (see table 3).

Total uptake of phosphorus

Figure 1 shows the influence of the various parts of mature barley plants added to two soils on the total uptake of phosphorus by rye grass during the second cutting period. These data were selected for plotting because they represent, on the one hand, uptake of phosphorus in a soil of high phosphorus fertility level (Pima clay loam) and, on the other hand, uptake from a phosphorus-"poor"

TABLE 4
Phosphorus absorbed per pot by rye grass from soil and from various barley materials

TREATMENT	SOIL*	TOTAL PHOSPHORUS ABSORBED	ABSORBED PHOSPHORUS DERIVED FROM TREATMENT†	ABSORBED PHOSPHORUS FROM SOIL
		<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>
Young hay	McClellan (v)	14.41	5.20	9.21
	McClellan (c)	8.17	4.42	3.75
	Pima (v)	56.24	9.10	47.14
Medium hay	McClellan (v)	12.51	4.10	8.41
	McClellan (c)	8.20	3.92	4.10
Mature straw	McClellan (v)	11.05	2.87	8.18
	McClellan (c)	7.69	3.15	4.54
	Pima (v)	31.80	3.99	27.81
	Verde (c)	5.61	1.65	3.96
	Mohave (c) 0-6 inches	8.78	1.73	7.05
	Mohave (c) 6-12 inches	8.13	1.71	6.42
Roots of medium hay	McClellan (v)	8.56	2.10	6.46
	McClellan (c)	5.75	1.89	3.86
Roots of mature straw	McClellan (v)	5.56	1.42	4.14
	McClellan (c)	4.46	1.31	3.15
	Pima (v)	24.82	1.97	22.85
Grain flour	McClellan (v)	12.01	2.80	9.21
	McClellan (c)	7.45	1.97	5.48
	Pima (v)	32.25	2.04	30.21
Hulls	McClellan (v)	12.89	4.85	8.04
	McClellan (c)	8.42	3.76	4.66
	Pima (v)	41.03	7.97	33.06
	Verde (c)	7.48	3.39	4.09
	Mohave (c) 0-6 inches	10.11	3.34	6.77
	Mohave (c) 6-12 inches	7.95	2.59	5.36
Chaff and awns	McClellan (v)	13.76	5.55	8.21
	McClellan (c)	7.25	4.33	2.92
	Pima (v)	35.38	8.06	27.32
	Verde (c)	7.43	3.46	3.97
	Mohave (c) 0-6 inches	10.34	3.64	6.70
	Mohave (c) 6-12 inches	6.23	2.51	3.72
Liquid H ₃ PO ₄	McClellan (v)	10.89	4.09	6.80
	McClellan (c)	5.64	2.81	2.83
	Pima (v)	41.05	7.63	33.42
	Verde (c)	6.97	3.29	3.68
	Mohave (c) 0-6 inches	9.09	2.60	6.49
	Mohave (c) 6-12 inches	8.10	2.29	5.81

* v = virgin; c = cultivated.

† Application of 9.9 mgm. phosphorus per pot either as plant material or liquid phosphoric acid fertilizer. Two cuttings only are shown in this table.

soil (McClellan clay loam). The figure distinguishes the amount of phosphorus derived from the soil from that derived from the barley materials. In the poorer McClellan soil, the total uptake was slightly greater under the straw treatment than under the H_3PO_4 treatment. Most of this increase was made at the expense of soil phosphorus.

In all but one instance, the total uptake from treatments was greatest in the soil highest in available phosphorus and general fertility, according to data in table 4. Except for the barley roots and grain, the data on total uptake indicate that the barley plant materials supplied the rye grass with at least as much available phosphorus as did the liquid H_3PO_4 (see table 4). A greater amount of phosphorus was derived from the McClellan soil when plant residues were

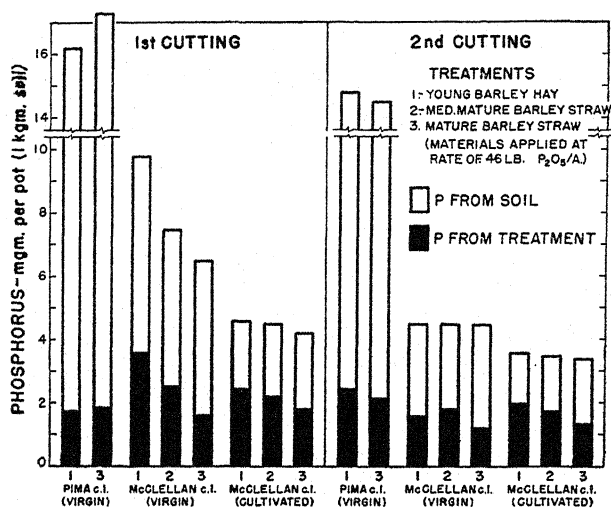


FIG. 2. TOTAL PHOSPHORUS UPTAKE FROM BARLEY HAY AND STRAW BY THE FIRST AND SECOND CUTTINGS OF RYE GRASS IN THREE DIFFERENT SOILS

present than when inorganic phosphorus as H_3PO_4 was present. On the other hand, figure 1 shows that in Pima clay loam, a soil high in organic matter, the grass receiving barley residue contained more soil phosphorus in two cases and less soil phosphorus in three cases than did plants receiving H_3PO_4 .

Influence of nitrogen applications on yield and total phosphorus uptake

Nitrogen may have had some influence on the yield and hence on the total phosphorus taken from all sources. The nitrogen percentages of the plant materials in order of decreasing values are: barley grain, straw, hulls, chaff and awns, and roots. Total phosphorus taken up by the rye grass decreased in this same order in the McClellan soil and except for the straw treatment, the order was the same in Pima clay loam.

The virgin Pima and McClellan and cultivated McClellan soils differ in total amount of phosphorus taken up by the grass. The soils having a greater quantity

of available phosphorus and total nitrogen yielded a greater total amount of phosphorus to the rye grass per unit of soil regardless of treatment. Figure 2 shows that the differences among soils, under the same treatment, are principally due to differences in phosphorus taken from the soil

DISCUSSION

A high proportion of the phosphorus of the barley plant materials, except grain, was found to be in the inorganic form. The extent of utilization of the organic and inorganic forms separately by the rye grass is not known. The phosphorus absorbed by the rye grass could have come primarily from the inorganic source, since seldom did the total uptake of the phosphorus from the plant residues exceed the amount added as the inorganic form. The young barley hay and medium mature straw were utilized to at least as great an extent as was liquid H_3PO_4 whereas the mature straw, found to have nearly as much inorganic phosphorus as did the younger straws, was clearly utilized to a lesser extent than was H_3PO_4 . This would indicate that some factor other than quantity of inorganic phosphorus as determined by the Pons and Guthrie (8) method influences the utilization. It may be speculated that changes in the nature of the major plant constituents of the barley materials at different stages of maturity influence the uptake of phosphorus from the tissues either indirectly by the effect on microbial activity in mineralization or directly by physically interfering with accessibility of the phosphorus for plant root absorption. The data indicate, nevertheless, that the inorganic phosphorus of different plant residues, when placed in a soil, is not equally available to a crop such as grass.

Analyses show that the phosphorus of barley grain flour is almost wholly organic. Only 15 per cent inorganic phosphorus could be extracted with cold trichloroacetic acid. Despite the high organic phosphorus content, the percentage utilization of the flour phosphorus was nearly as great as that of mature barley straw, found to have an inorganic phosphorus content of 82 per cent. The principal organic phosphorus constituent of flour is phytin. The ready availability of the grain phosphorus is surprising in view of the very high organic phosphorus content of the grain and the reports (2, 10) that organic phosphorus is fixed in soils in the form of phytates.

A total of 9.98 mgm. of phosphorus was added per pot as barley grain flour. Of this amount, 3.64 mgm. was taken up by three cuttings of rye grass growing on the virgin McClellan clay loam. Since the phosphorus of the grain is 15 per cent inorganic, only 1.50 mgm. of the phosphorus added could be inorganic. Thus 2.14 mgm. organic phosphorus must have been utilized by the grass if all the inorganic phosphorus were considered to have been used.

Except for the liquid H_3PO_4 treatment, the percentage of phosphorus (P) in the grass derived from the various barley straw sources was about the same the second cutting as the first. Utilization of the phosphorus of liquid H_3PO_4 was clearly less than that of the straw sources in four of six soils for the second cutting of grass. Moreover, the total phosphorus uptake by rye grass during the second period fell off markedly from that of the first in H_3PO_4 treatment in contrast to

that of all barley treatments. These findings would imply that liquid H_3PO_4 becomes less available with time and is more susceptible to being fixed in calcareous Arizona soils than is phosphorus of crop residues.

Another rather interesting feature of the investigation is the influence of nitrogen on uptake. The treatment of the McClellan soils, having previously received barley materials and liquid H_3PO_4 , with 100 pounds of nitrogen per acre decidedly increased rye grass yield and total phosphorus uptake from all sources but did not change the proportion of phosphorus in the plant derived from the different sources over that of the early cuttings.

SUMMARY

Barley materials of three different stages of maturity and from different parts of the plant were added to six different soils in the greenhouse at rates equivalent to 46 pounds of P_2O_5 per acre, and the utilization by rye grass was compared with that of liquid H_3PO_4 .

The availability of the phosphorus of the barley residues to rye grass appeared to be inversely related to the stage of maturity. Young and medium mature barley hay appeared to supply phosphorus to rye grass to about the same extent as did liquid H_3PO_4 . The latter, however, appeared to be more available to rye grass than was mature barley straw and roots.

Utilization of phosphorus from various parts of the barley plant incorporated in calcareous soils was not the same.

The proportion of inorganic to organic phosphorus found in the various barley plant parts appeared to have little influence on the utilization of the plant phosphorus by rye grass.

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CLAY MINERALS OF SOUTH AFRICAN SOIL GROUPS: I. LATERITES AND RELATED SOILS

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Received for publication October 15, 1951

The soils of the Union of South Africa and surrounding territories have been comprehensively described (5) on the basis of data collected during a reconnaissance soil survey of the subcontinent. The soils were classified into groups and subgroups according to their characteristic morphology as influenced by parent material, climate, vegetation, topography, and other soil-forming factors. In collecting the soil data, particular attention was paid to soils developed under normal soil-formative influences.

A soil is composed of particles varying in size from that of coarse sand to that of clay with an admixture of gravel and stones in many instances. The coarser material forms a relatively inert framework of unweathered minerals and rock fragments. The case is quite otherwise with the clay or colloid fraction ($<2 \mu$), since this fraction consists mainly of products of chemical weathering of silicates to clay minerals, which, together with organic matter, constitute the so-called humus-clay complex. This fraction normally reflects the chemical changes that have taken place during soil formation. In addition, it is responsible for many characteristic physical properties such as retention of moisture, expansion on wetting, shrinkage on drying, plasticity, and cohesion. Joffe (3) states correctly: "There is hardly a chemical, physical, and morphological property of the soil body that is not influenced by these minerals. One may venture to state that there is not a problem of soil science that is not in one way or another associated with the reactions exhibited by clay minerals."

Obviously, much is to be gained from a knowledge of the mineralogical constitution of soil colloids and from comparison of colloids from soils of different groups. In the study of soil groups and subgroups of South Africa, soil samples from representative profiles were subjected to mechanical and chemical analyses, and, in selected cases, base-exchange and *S*-values were determined. In addition, soil colloids were analyzed and their derived molar ratios, $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-Fe}_2\text{O}_3$, and $\text{SiO}_2\text{-R}_2\text{O}_3$, determined. Use of such ratios is well established, but in their interpretation there is divergence of opinion. Thus, some writers consider that the ratio of most significance is $\text{SiO}_2\text{-R}_2\text{O}_3$, while others are of the opinion that $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratios supply more information with regard to clay mineral constituents of the tropical and subtropical soils. Fe_2O_3 in certain tropical and subtropical soils is considered as adventitious material and the combined silica occurs mainly as aluminum silicates; even when both are present in a clay

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mineral such as a montmorillonite, their respective functions differ widely. In fact, all that can be said with any certainty is that, if kaolinite is the only clay mineral present and all silica is combined, the $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio gives a good idea of the possibility of decomposition of the clay minerals of the kaolin group to free alumina. When the ratio is less than 2.0, as in colloids of lateritic soils, it is fairly safe to postulate that the main minerals present are those of the kaolin group, gibbsite, and iron oxide.

At the time of the study it was realized that direct identification of minerals in soil colloids by such methods as differential thermal analysis and x-ray diffraction was most desirable, but the necessary equipment was not available. The object of the present series of papers is to report the application of such methods to clay fractions of the samples used for the original monograph.

This first paper covers laterites and related soils, classified in the monograph as (i) laterites, (ii) lateritic red earths, (iii) lateritic yellow earths, (iv) gray ferruginous lateritic soils, (v) brown to reddish brown ferruginous lateritic soils. Of these, the first three and the last two fall into quite distinct groups. As summarized by Robinson (7), a great deal of controversy is centered round the definition of a "laterite." The soils in the first three classes have free internal drainage and are free from concretions, and kaolinite is partly decomposed to free alumina as shown by $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratios of less than 2.0. By some writers, these are regarded as truly lateritic, but Robinson suggests the term "ferrallitic." The soils in the latter two classes have developed under lower rainfalls and are less completely leached. Internal drainage has been indifferent, giving rise to temporary waterlogged conditions and extensive formation of ferruginous concretions. According to Pendleton (6) and also to Robinson, this is the group to which the term "lateritic" should be applied. To a great extent, the two uses of the term are mutually exclusive. Since no finality with regard to the use of the term has been reached and since a revision of classification is not the purpose of this paper, the present writers would prefer to confine themselves to the original group designations of the monograph. In that publication the term "laterite" in the first three soil groups has been applied more particularly to the weathered rock product formed by the leaching of rocks, whereby the bases and much of the silica are removed, leaving a residue containing alumina uncombined with silica (2).

As readers of these articles may not have ready access to the original monograph, a brief recapitulation of morphological features is given for each sample, together with such analytical data as are relevant to the present discussion.

TECHNIQUES AND INTERPRETATION OF DATA

Differential thermal analysis

The differential thermal apparatus used for this investigation is described in detail in another paper (1).

X-ray diffraction investigation

X-ray patterns were obtained with a Norelco Geiger-counter x-ray spectrometer, type 12021, with $\text{CoK}\alpha$ radiation ($\lambda = 1.7902$ a.u.), and an automatically recording Brown Elektronik strip-chart potentiometer.

The x-ray diffraction patterns for kaolinite and halloysite are well contrasted, but soil colloids may give intermediate diagrams. The distinction between the two, if made at all, is based on the fact that the basal spacing is 7.14A. for kaolinite and 7.4 for halloysite, and that kaolinite diffraction lines at 2.3 and 2.5A., which are themselves sometimes resolved into doublets, may appear as one broad band in halloysite.

On the whole, identification of kaolinite, which was the clay mineral in nearly all the present soils, and of gibbsite gave no trouble. Kaolinite normally occurs in a well-crystallized state and gives both a well-defined differential thermogram and a large number of characteristic peaks on an x-ray powder diagram. The same is true for gibbsite. Differential thermograms of gibbsite show a distinctive endothermal peak at 330°–350°C. Even when a large exothermal "hump" appeared in this range, a little gibbsite produced a sharp depression.

Identification of iron oxides, however, was most unsatisfactory. As hematite gives no effect on a differential thermogram, reliance had to be placed upon x-rays. This was also the case with the hydrates goethite and lepidocrocite, since these give endothermal peaks in the same region as gibbsite and hence tend to be masked by it. Iron oxides in all their forms proved to be much the least crystalline of the constituents of the soil colloids. In such cases, x-ray powder diagrams are reduced to a few very broad peaks of relatively low intensity. When kaolinite and gibbsite are present, most of the few peaks which should still appear coincide with much stronger peaks given by these minerals. The net result was, for instance, that, with 20 per cent iron oxide in the sample, identification of hematite had to rest upon a single peak in a position which could not be confused with other constituents. Sometimes such a peak was of such low intensity that its reality was doubtful, and the sample was treated with strong HCl and run again. If the peak disappeared, it was considered to be real and to be due to iron oxide. Identification of goethite and lepidocrocite was more difficult, and, though reported as goethite, no evidence was obtained in any case as to which of these two forms was present. If kaolinite and hematite were present, no definite identification of hydrous iron oxides could be made, so that the possibility of their presence cannot be excluded in any case. The problem of the form of iron oxide is a very interesting one, and more work upon it is under way.

RESULTS

The lateritic earths

Nearly all the soil colloids analyzed in the original monograph were examined. As the results were largely repetitive, only profiles of special significance were selected for discussion. All profiles that were omitted gave results in complete accord with those selected. Similarly, a record of all samples from a profile has not been considered necessary where the samples omitted merely duplicated results. An omission which should be recorded is that surface samples, which almost invariably gave poor differential thermograms due to rather large amounts of organic matter and, in some cases, to presence of fertilizers, were not included.

Laterites. This soil group, derived from dolomite, has good surface drainage

and has developed under high summer rainfall and temperatures and fairly dry and mild winters.

The well-developed residual soil is deep and has as

- (a) surface soil—brown to yellowish brown, soft, crumbly clay, containing about 6 per cent organic material and 9–12 inches thick;
- (b) subsoil—reddish brown, slightly granular to crumbly clay, 12 inches thick;
- (c) substratum—dull reddish brown to brownish red, crumbly clay, many feet thick.

The clay content ($< 2 \mu$) of the various horizons of the profiles varies from 53 to 69 per cent, and the soil colloid consists almost entirely of silica, alumina, iron oxide, and titania. The soil contains no mottled or gray zones and no hard crust of iron oxides and alumina on the surface or embedded anywhere in the profiles.

TABLE 1
Analytical and derived data for laterites

PROFILE AND SAMPLE NO.	DEPTH	CLAY FRAC- TION	ANALYSIS OF OVEN-DRIED COLLOID FRACTION					BASE EXCHANGE (<i>S</i> -VALUES) PER 100 GM. DRY SOIL
			SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂ R ₂ O ₃	SiO ₂ Al ₂ O ₃	
	<i>in.</i>	%	%	%	%			<i>me.</i>
Sabie I: dolomite; rainfall 48 inches a year								
A 8514	24–48	68.7	25.06	28.92	41.73	0.70	1.01	—
Sabie II								
A 8487	36–48	60.6	13.54	32.16	50.67	0.32	0.45	1.0

Profiles of two localities were sampled. As no marked differences with depth were observed, only one sample from each locality is reported here. Analytical data are given in table 1. The low SiO₂-Al₂O₃ ratios indicate that weathering has passed beyond formation of clay minerals and has decomposed these extensively to free alumina. This process, accompanied by leaching of silica and of easily soluble material, is regarded by one group of pedologists as characteristic of laterization. In accordance with the system of Martin and Doyne (4), the Sabie profiles are grouped as laterites because the SiO₂-Al₂O₃ ratio lies considerably below 1.33. The negligible base exchange of the soils was in accord with a composition consisting mainly of uncombined iron and aluminum oxides.

The base exchange—*S*-values—was determined by first leaching the soils with *N* NH₄Cl and distilling the leached soils with caustic soda to determine their NH₄-absorbed or *S*-values.

The present work has supported these deductions. Differential thermograms in figure 1 show a pronounced endothermal peak at about 350° for gibbsite, together with peaks for kaolinite. The relatively lower proportion of gibbsite in A 8514 is in accord with the higher silica percentage in table 1. It may be noted that silica percentages in samples at high levels of the Sabie I profile were considerably smaller.

X-ray diffraction confirmed the presence of gibbsite and kaolinite and also showed hematite. These were the only minerals that could be identified.

Lateritic red earths. These soils, developed under high summer rainfall and temperatures and relatively dry and moderately mild winters, are derived from sandstones, shales, conglomerates, acid and basic igneous and intermediate rocks with good surface drainage. The well-developed residual soils are deep and possess similar physical and chemical composition and morphological characteristics despite the diverse parent material.

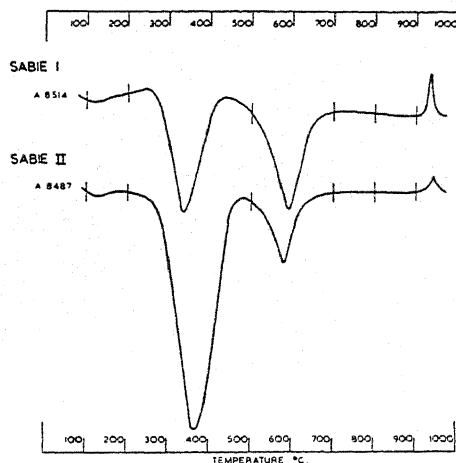


FIG. 1. DIFFERENTIAL THERMAL CURVES OF LATERITES—SABIE I AND SABIE II

The mature soils with good internal drainage have as

- (a) surface soil—dark brown, crumbly to granular clay, 10 inches thick;
- (b) subsoil and substratum—brownish red, crumbly clay, varying in thickness from 2 to more than 9 feet with no change in color, texture, and structure;
- (c) substratum—underlying the above, a yellowish brown, crumbly clay loam to loam of unknown thickness.

The lateritic red earths possess good water-absorbing and retaining capacities, are well leached of all soluble constituents, contain 0.20 per cent total nitrogen, and have approximately 4 per cent organic matter in the surface soil.

The ultimate analysis of the colloids indicates that silica, iron oxide, and alumina form the main constituents. No concretionary material consisting of iron oxide and alumina is accumulated anywhere in the profile.

The samples in table 2 were selected to illustrate profiles of soils derived from a number of parent materials under different ranges of rainfall intensity. In the table are included percentages of clay fraction in total soil, base exchange (*S*-values) of total soil, SiO_2 and R_2O_3 percentages in the oven-dried colloid fraction, and derived molar ratios. The $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratios for the colloid fractions of these soils were uniformly low, indicating their lateritic character. In con-

formity with this, base exchange is low, though higher than for the laterites in table 1.

Differential thermograms are shown in figures 2, 3, and 4. Since a measure of laterization is breakdown of kaolinite to free alumina, the profiles in these

TABLE 2
Analytical and derived data for lateritic red earths

PROFILE AND SAMPLE NO.	DEPTH	CLAY FRACTION	ANALYSIS OF OVEN-DRIED COLLOID FRACTION					BASE EX- CHANGE (S-VAL- UES) PER 100 GM. DRY SOIL
			SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂ R ₂ O ₃	SiO ₂ Al ₂ O ₃	
	<i>in.</i>	<i>%</i>	<i>%</i>	<i>%</i>	<i>%</i>			<i>me.</i>
Krugersdorp: diabase; rainfall 27 inches a year								
A 9037	6-22	59.1	42.81	19.97	32.52	1.60	2.22	—
A 9039	60-84	42.1	45.63	20.88	28.54	1.84	2.70	—
A 9040	84-144	11.8	47.28	21.23	27.39	1.96	2.92	—
Johannesburg: granite; rainfall 29 inches a year								
B 98	30-60	35.7	47.17	8.11	42.19	1.69	1.89	3.2
B 99	60-90	22.3	47.74	7.31	42.08	1.73	1.92	2.8
Louis Trichardt: sandstone; rainfall 35 inches a year								
B 26	0-10	53.9	36.51	23.84	36.06	1.21	1.72	5.2
B 28	24-48	66.4	36.27	23.11	37.22	1.18	1.65	4.4
Wolkberg: Black Reef series*; rainfall 45 inches a year								
A 9443	48-60	25.6	37.76	18.97	38.19	1.27	1.67	1.6
Louwsburg: dolerite; rainfall 32 inches a year								
A 8307	12-30	59.6	32.01	32.12	30.93	1.05	1.75	6.6
A 8309	30-44	33.2	28.55	35.84	30.29	0.90	1.59	6.8
Tzaneen: granite; rainfall 38 inches a year								
A 8084	6-10	47.5	35.51	22.22	36.39	1.18	1.65	6.8
A 8090	60-72	64.6	34.18	23.68	38.29	1.08	1.50	3.6
A 8094	108-120	36.3	31.42	34.61	28.81	1.40	1.85	—
Mbabane: granite; rainfall 45 inches a year								
A 8314	48-84	57.0	35.38	17.71	42.49	1.11	1.41	3.2
A 8316	100-132	17.9	44.23	18.98	32.64	1.67	2.29	3.4

* A series of sedimentary rocks consisting of quartzites, sandstones, graywackes, and conglomerates.

figures and also in table 2 are arranged in order of intensity of gibbsite peaks, at about 350°C. This conforms closely to the order of SiO₂-Al₂O₃ ratios, which are again closely correlated with the rainfall normals, indicating that rainfall and temperatures are of more importance to laterization than is the parent material.

Of the Krugersdorp and Johannesburg profiles, only one sample each shows a slight indication of gibbsite, notably the sample with the smallest $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio in each case. As this ratio in all samples is very close to 2.0, corresponding to kaolinite, this observation is to be expected. These soils, in fact, lie at the borderline of the lateritic group, indicating that rainfall is barely sufficient to produce the necessary degree of decomposition and leaching for laterization.

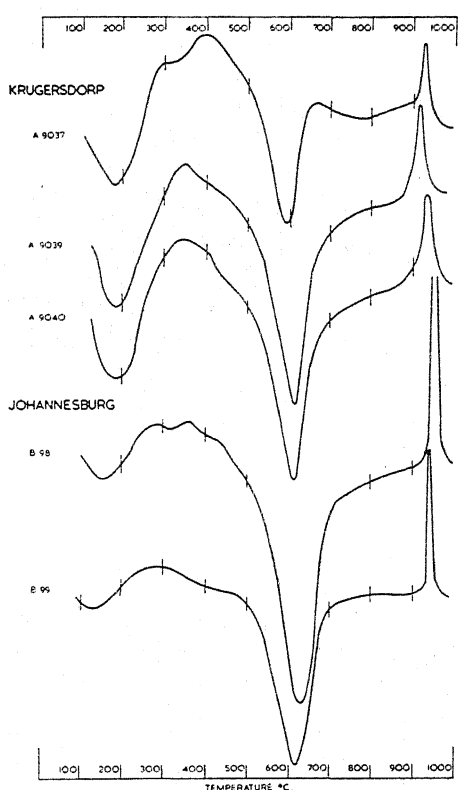


FIG. 2

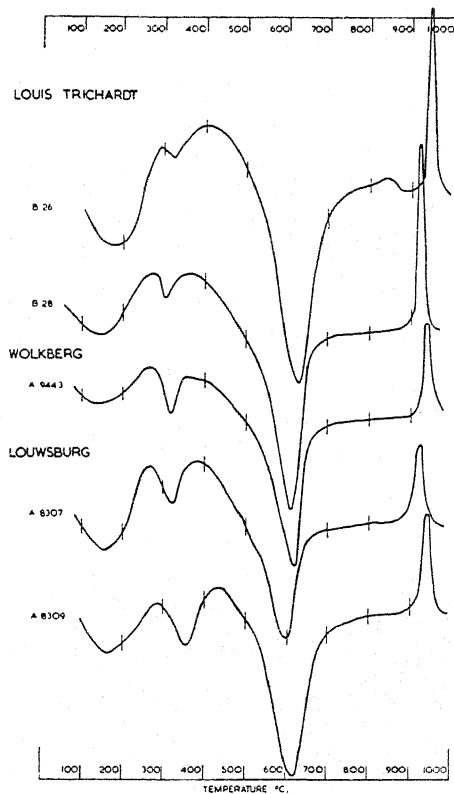


FIG. 3

FIG. 2. DIFFERENTIAL THERMAL CURVES OF LATERITIC RED EARTHS—KRUGERSDORP AND JOHANNESBURG

FIG. 3. DIFFERENTIAL THERMAL CURVES OF LATERITIC RED EARTHS—LOUIS TRICHARDT, WOLKBERG, AND LOUWSBURG

With respect to the remaining profiles, it is to be noted that the deepest samples from Tzaneen and Mbabane give relatively high $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratios and correspondingly small gibbsite peaks. These samples are close to the decomposing rock and are therefore less well developed.

Interpretation of x-ray data is given in table 3. Although intensities of hematite peaks were low for the percentage of iron oxide, they were sufficient for identification of this mineral in all of the red earths. In the Johannesburg colloids, the

percentage of iron oxide was very low, and hematite peaks were very weak. In the lower level for this profile, mica is listed in the "doubtful" column. On the whole, differential thermograms gave a more sensitive indication of variations in the proportion of gibbsite present.

From the foregoing examples, it would seem that laterization starts under the subtropical conditions prevailing in South Africa when the normal rainfall

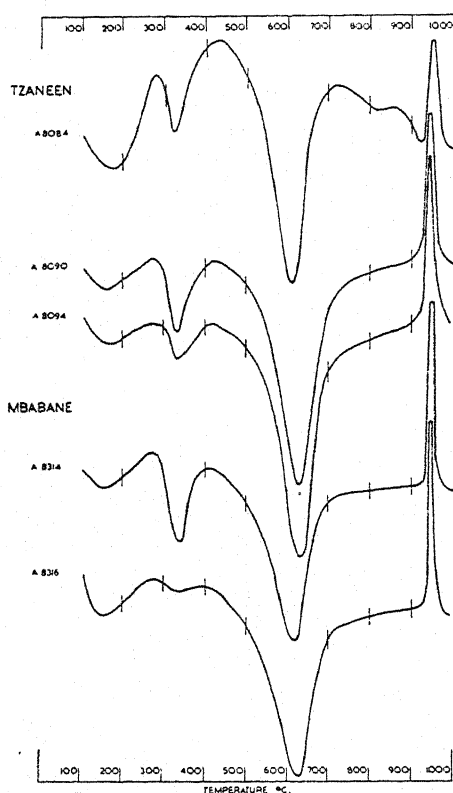


FIG. 4

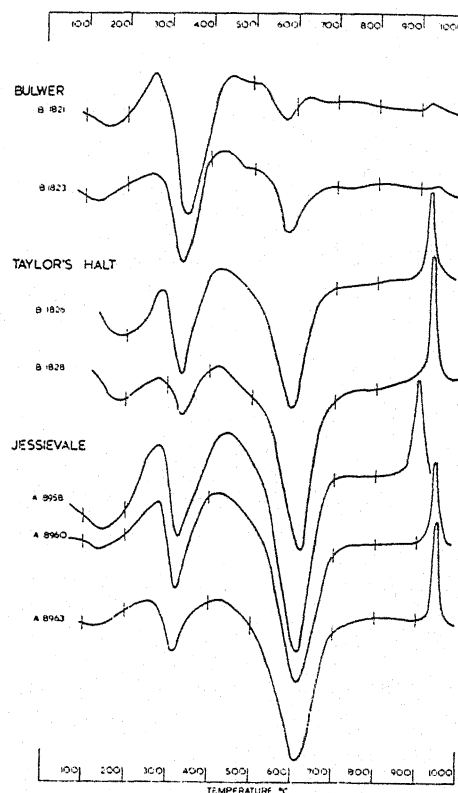


FIG. 5

FIG. 4. DIFFERENTIAL THERMAL CURVES OF LATERITIC RED EARTHS—TZANEEN AND MBABANE

FIG. 5. DIFFERENTIAL THERMAL CURVES OF LATERITIC YELLOW EARTHS—BULWER, TAYLOR'S HALT, AND JESSIEVALE

exceeds about 30 inches a year, provided surface drainage and internal drainage are both good.

The extensive decomposition produced under these conditions more or less obliterates the influence of the parent material. It is widely believed that basic igneous rocks such as dolerite and diabase laterize more easily at a lower rainfall than do acid igneous rocks such as granites. Yet the gibbsite content of soil colloids in table 2 is much the same for soils from both acid and basic rocks under

similar rainfall. Only the conglomerate of the Black Reef series—Wolkberg profile—requires a higher rainfall to produce comparable results.

Lateritic yellow earths. This soil group occurs mainly in west-central Natal with outliers in the Cape Province and in Transvaal. The soils have developed under high summer rainfall and temperature and relatively dry and fairly cold winters.

The normal soils, whether derived from acid or basic igneous or sedimentary rocks, possess closely related morphological characteristics and chemical composition, are generally deep, and have good surface and internal drainage.

TABLE 3
X-ray results for lateritic red earths

PROFILE AND SAMPLE NO.	DEFINITE	WEAK	DOUBTFUL
Krugerdsorp			
A 9037	Kaolinite, hematite		
A 9039	Kaolinite, hematite		
A 9040	Kaolinite, hematite		
Johannesburg			
B 98	Kaolinite	Hematite	Gibbsite
B 99	Kaolinite	Hematite	Mica
Louis Trichardt			
B 26	Kaolinite, hematite	Gibbsite	
B 28	Kaolinite, hematite	Gibbsite	
Wolkberg			
A 9443	Kaolinite	Gibbsite, hematite, quartz	
Louwsburg			
A 8307	Kaolinite, hematite	Gibbsite	
A 8309	Kaolinite, hematite	Gibbsite	
Tzaneen			
A 8084	Kaolinite, gibbsite, hematite		
A 8094	Kaolinite, gibbsite, hematite		
Mbabane			
Mbabane			
A 8314	Kaolinite, gibbsite, hematite		
A 8316	Kaolinite, hematite	Gibbsite	

The well-developed soil has as

- (a) surface soil—dark brown, crumbly to granular clay, containing more than 5 per cent of organic material, and 10 inches thick;
- (b) subsoil—yellowish brown, crumbly clay, 16–24 inches thick;
- (c) substratum—reddish brown, crumbly clay, many feet thick.

These soils have excellent water-absorbing and -retaining capacities. Their colloids show a remarkable uniformity of chemical composition; they consist almost entirely of silica, alumina, and oxides and hydroxides of iron. There is no concretionary material either as hardpan or as loose concretions anywhere in the profiles.

The morphological characteristics, except the color, of the red and yellow earths are closely related. This is borne out by analyses of colloid fractions from representative profiles in table 4. The $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratios indicate an advanced stage of laterization. Actually, the Taylor's Halt profile is an intrazonal red earth but occurs in a yellow earth zone.

The areas of the gibbsite peaks on the differential thermograms in figure 5 are in full agreement with a degree of laterization between that of laterites (fig. 1) and of lateritic red earths (figs. 2, 3, 4). In all these profiles, the deepest samples have larger $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratios and smaller peaks, due to contiguity to the parent rock and a consequent lower degree of maturity.

TABLE 4
Analytical and derived data for lateritic yellow earths

PROFILE AND SAMPLE NO.	DEPTH	CLAY FRAC- TION	ANALYSIS OF OVEN-DRIED COLLOID FRACTION					BASE EXCHANGE (S-VALUES) PER 100 GM. DRY SOIL
			SiO_2	Fe_2O_3	Al_2O_3	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	
	<i>in.</i>	%	%	%	%			<i>me.</i>
Bulwer: sandstones and shales; rainfall 42 inches a year								
B 1821	24-38	57.0	26.00	21.19	47.48	0.72	0.93	4.0
B 1823	60-72	44.0	34.40	18.98	39.56	1.13	1.47	6.0
Taylor's Halt: dolerite; rain- fall 42 inches a year								
B 1826	24-43	74.3	30.56	24.33	41.22	0.91	1.26	4.6
B 1828	62-72	70.4	37.89	21.10	37.33	1.21	1.70	8.6
Jessievale: granite; rainfall 34 inches a year								
A 8958	1-4	40.6	40.69	9.11	48.57	1.26	1.41	4.4
A 8960	10-16	49.1	40.04	8.41	49.22	1.24	1.37	2.6
A 8963	50-74	39.1	42.12	9.57	46.74	1.35	1.52	2.2

X-ray data are summarized in table 5. The Bulwer profile proves to be of particular interest because no evidence of kaolinite is found, but there are weak indications of a micaceous mineral. This accords with the differential thermograms in figure 5, since the rather weak peaks observed in the vicinity of 600°C. and 900°C. correspond more nearly to the clay mineral illite than to kaolinite. As the $\text{SiO}_2\text{:Al}_2\text{O}_3$ for a typical illite is much larger than 2.0, a given $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio in this soil colloid corresponds to a considerably more complete decomposition of the clay mineral than when kaolinite is the clay mineral present. The relative intensities of the gibbsite and illite peaks in figure 5 are in accord with this.

The Bulwer profile also enabled identification of a hydrous iron oxide, provisionally listed as goethite. This gave stronger peaks than hematite, which could also be identified, and probably accounts for the yellow color. To some extent, this identification of goethite must be listed as a fortunate accident,

since its presence could not have been proved if a large percentage of kaolinite had been present.

In accord with its red color, the Taylor's Halt profile contained iron oxide as hematite. The Jessievale profile, which had a low percentage of iron oxides, gave only doubtful indication of their presence. It seems probable that the yellow color, in contrast to the color of red earths, is due to a preponderance of ferric oxide in hydrated form, as goethite, over unhydrated hematite, though the evidence is not so satisfactory as might be desired, because of difficulties in identification of goethite, when kaolinite, gibbsite, and hematite are also present.

Despite their close relationship, yellow and red earths are classified separately, because they are considered to be formed under somewhat different climatic

TABLE 5
X-ray results for lateritic yellow earths

PROFILE AND SAMPLE NO.	DEFINITE	WEAK	DOUBTFUL
Bulwer			
B 1821	Gibbsite	Goethite, mica	Hematite
B 1823	Gibbsite	Goethite, mica, hematite	
Taylor's Halt			
B 1826	Kaolinite, gibbsite, hematite		Mica
B 1828	Kaolinite, hematite	Gibbsite, mica	
Jessievale			
A 8958	Kaolinite, gibbsite		Iron oxide
A 8960	Kaolinite, gibbsite		Iron oxide
A 8963	Kaolinite, gibbsite		Iron oxide

conditions. Yellow earths appear to correspond to colder winters, the low temperatures being adverse to dehydration of hydrous iron oxides to hematite. Iron oxide seems also to be more mobile and is more readily leached from the soil; for example, the Jessievale colloid, with about 9 per cent Fe_2O_3 , is derived from a similar parent rock to that of the Mbabane colloid, with about 18 per cent Fe_2O_3 .

Ferruginous lateritic soils

The gray and the brown ferruginous lateritic soils occur in regions adjacent to the lateritic earths. They have developed under lower rainfalls, namely, 22 to 30 inches a year, and therefore leaching has been much less severe and the progress of weathering has been very considerably modified. In particular, they differ from the lateritic earths in that the character of the soil is greatly influenced by the parent rock. The term "ferruginous" in their name refers to characteristic presence of iron oxide concretions.

Gray ferruginous lateritic soils. These soils are always associated with geological formations, for example, red and old granites and sandstones, that produce light-textured soils under certain rainfall conditions. The surface relief consists of a succession of gently undulating ridges with well-defined watercourses. The vegetation is that of a typical savanna region, consisting of grasses, evergreen and deciduous trees, bushes, and thorns.

Most of the rain falls during the hot summers; the winters are fairly dry and very mild. The surface drainage is good, but the internal drainage is impeded by a fairly impervious deflocculated clay horizon relatively near the surface, creating temporary internal waterlogging. This latter factor plays an important role in

TABLE 6
Analytical and derived data for gray ferruginous lateritic soils

PROFILE AND SAMPLE NO.	DEPTH	CLAY FRACTION	ANALYSIS OF OVEN-DRIED COLLOID FRACTION					BASE EXCHANGE (S-VALUES) PER 100 GM. DRY SOIL
			SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂ R ₂ O ₃	SiO ₂ Al ₂ O ₃	
	<i>in.</i>	%	%	%	%			<i>me.</i>
Letaba Station: granite; rainfall 30 inches a year								
A 8077	4-12	17.7	49.99	4.64	40.49	1.95	2.09	3.0
A 8081	44-55	27.0	46.50	9.85	37.82	1.78	2.08	6.0
Pyramid: sandstone; rainfall 26 inches a year								
A 6072	24-32	7.0	46.66	15.16	32.90	1.85	2.40	1.3
A 6075	62-70	9.2	52.42	11.49	30.38	2.35	2.92	1.1
Klipkop: granite; rainfall 22 inches a year								
A 8931	18-30	20.5	44.44	19.64	30.91	1.73	2.43	7.6
A 8933	36-60	27.0	50.18	11.57	33.38	2.09	2.55	10.1

the formation of these soils and is responsible for their characteristic morphological features.

The normal well-developed soil is of residual origin and has as

- surface soil—gray gravelly sand with coherent structure, overlying light gray, friable sandy gravel (quartz grit and few ferruginous concretions);
- subsoil—light brown, mottled black and brown, gravelly (ferruginous concretions) clayey sand, resting on a brown ferruginous hardpan, called "ouklip";
- substratum—mottled deflocculated clayey material with occasional iron oxide concretions embedded in it.

In this soil group and also in the brown to reddish brown ferruginous lateritic soils it is noteworthy that the clay fractions do not contain all the chemical reactive colloidal material of the soil, because an appreciable amount of its iron content occurs as ferruginous concretions and hardpan which would not appear in the colloids. Another point to be noted is the low percentage of the clay fraction, in strong contrast to the lateritic earths.

Analyses are given in table 6, differential thermograms in figure 6, and x-ray results in table 7. Quartz and mica occur in considerable quantities in each of the samples. As the only clay mineral shown by the differential thermograms was kaolinite, it would seem that "mica" is not illite but is truly mica which has remained unchanged in weathering of the parent rocks. In the Klipkop profile, the base-exchange capacity of the soil in relation to the percentage of clay is rather high, and the micaceous constituent may be illite.

In contrast to the lateritic earths, $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratios here give a misleading indication of mineralogical constitution, due to presence of silica as quartz and mica. Thus, though these ratios were above 2.0 in all cases, most of the samples contained some gibbsite, showing that weathering of clay minerals to free alumina had taken place.

TABLE 7
X-ray results for gray ferruginous lateritic soils

PROFILE AND SAMPLE NO.	DEFINITE	WEAK	DOUBTFUL
Letaba Station			
A 8077	Kaolinite, quartz, mica		Iron oxides
A 8081	Kaolinite, quartz, mica		Iron oxides
Pyramid			
A 6072	Kaolinite, quartz, mica	Hematite	Gibbsite
A 6075	Kaolinite, quartz, mica	Hematite, gibbsite	Gibbsite
Klipkop			
A 8931	Kaolinite, quartz, mica		Gibbsite
A 8933	Kaolinite, quartz, mica		Gibbsite

Brown to reddish brown ferruginous lateritic soils. These soils occur extensively in central Transvaal and northwest Natal. They form the transition region between the Highveld and Middleveld. The surface relief varies from gently undulating to hilly. The parent material comprises shales, quartzites, sandstones, dolomites, and acid and basic igneous rocks.

The vegetation is grass in the open and shrubs and grass in the broken country. Normal rainfall ranges from 20 to about 30 inches, and the precipitation occurs mainly during the summer months. The winters are relatively dry and rather cold.

The morphological features of the well-developed soils of this soil group vary considerably, being influenced by the underlying parent material. The following profile descriptions give an idea of the variations:

Soil derived from basic igneous rock

- (a) surface soil—dark reddish brown, crumbly clay, about 8 inches thick;
- (b) subsoil—reddish brown, crumbly clay with no color, texture, or structure change to a depth of 42 inches. It contains no concretions or hardpan in the profile.

Soil derived from shale

- (a) surface soil—brown, crumbly clay loam, containing a fair amount of quartz gravel, and 6 inches thick;

- (b) subsoil—coarse gravel (mainly uncemented iron oxide concretions) and shale fragments, 12 inches thick. Underlying this horizon is the comparatively undecomposed shale.

Soils derived from sandstone

- (a) surface soil—dark gray, crumbly sandy loam, 8 inches thick;
 (b) subsoil—yellowish brown, soft, crumbly sandy clay loam, 28 inches thick;
 (c) substratum—dark brown, compact ferruginous hardpan having the interstices between concretions filled with clay and sand.

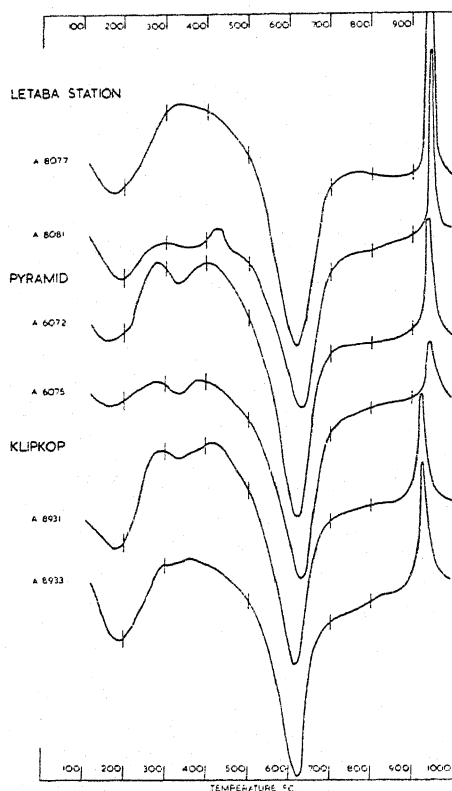


FIG. 6

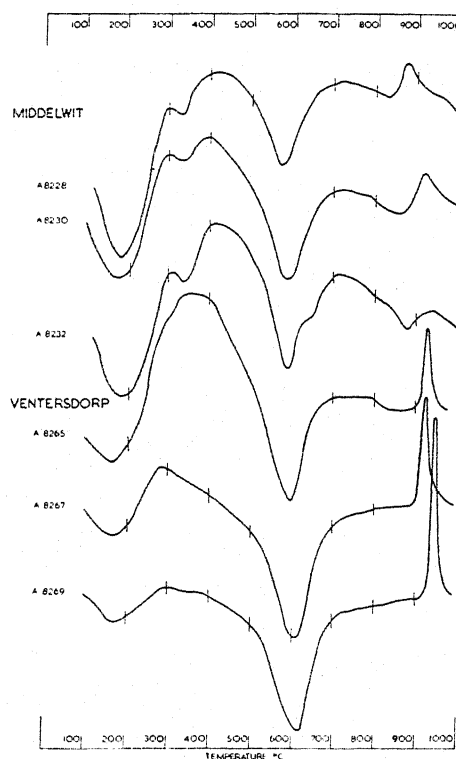


FIG. 7

FIG. 6. DIFFERENTIAL THERMAL CURVES OF GRAY FERRUGINOUS LATERITIC SOILS—LETABA STATION, PYRAMID, AND KLIPKLOP

FIG. 7. DIFFERENTIAL THERMAL CURVES OF BROWN TO REDDISH BROWN FERRUGINOUS LATERITIC SOILS—MIDDELWIT AND VENTERSDORP

In these soils the chemical composition and character of the parent materials determine the response to weathering under almost identical climatic conditions. The peculiarities and composition of the parent materials persist even in the characteristics of the well-developed soils.

In these soils, in spite of their apparent morphological differences, there is an underlying similarity in complete absence of carbonate of lime and presence of ferruginous (and manganiferous) concretions. In all cases, internal drainage

has been impeded by an impervious layer below the solum so that temporary waterlogged conditions may occur periodically just above this layer during heavy rains. This fluctuating water table produces anaerobic and reducing conditions by which the iron and in some instances manganese (Middelwit and Ventersdorp) in the soil are reduced to the more soluble forms. The soluble compounds

TABLE 8

Analytical and derived data for brown to reddish brown ferruginous lateritic soils

PROFILE AND SAMPLE NO.	DEPTH	CLAY FRAC- TION	ANALYSIS OF OVEN-DRIED COLLOID FRACTION					BASE EXCHANGE (S-VALUES) PER 100 GM. DRY SOIL
			SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂ R ₂ O ₁	SiO ₂ Al ₂ O ₃	
	<i>in.</i>	%	%	%	%			<i>me.</i>
Middelwit: dolomite; rainfall 22 inches a year								
A 8228	0-6	26.2	43.33	23.11	24.45	1.87	3.00	18.4
A 8230	12-24	17.7	39.10	25.46	21.84	1.74	3.04	14.3
A 8232	36-37	21.4	40.06	22.36	22.05	1.87	3.08	14.1
Ventersdorp: dolomite; rainfall 24 inches a year								
A 8265	0-6	11.6	42.57	15.92	33.05	1.67	2.18	4.1
A 8267	18-36	21.4	42.48	18.59	33.84	1.57	2.17	2.0
A 8269	54-66	37.0	41.44	17.82	30.84	1.66	2.27	3.3
Marikana No. 1: diabase; rain- fall 26 inches a year								
A 8679	0-10	44.3	45.58	13.35	37.36	1.68	2.06	13.8
A 8681	24-38	51.2	45.55	12.90	38.89	1.63	1.98	11.1
A 8683	48-61	37.6	47.60	10.99	39.28	1.74	2.05	16.3
Ermelo: shales and sandstones; rainfall 33 inches a year								
A 8293	20-36	32.3	39.32	16.50	41.97	1.27	1.59	3.4
A 8294	36-50	19.3	40.70	16.62	38.95	1.38	1.76	5.5
Marikana No. 2: diabase; rain- fall 26 inches a year								
A 8686	0-8	61.0	61.42	11.55	18.64	4.02	5.59	52.2
A 8688	23-36	60.6	62.49	11.99	18.20	4.09	5.82	56.5
A 8690	48-57	50.7	62.10	11.70	18.54	4.05	5.68	50.2
A 8692	63-84	6.6	57.81	16.05	16.24	3.71	6.06	16.8

produced by a change in moisture conditions in the soil are oxidized by the oxygen in the soil atmosphere, precipitated, and, on drying, dehydrated and indurated to form concretions and sometimes hardpans.

In gray ferruginous soils, the temporary waterlogging extends to the surface. In the brown soils it occurs in deeper layers, and, therefore, surface and subsoil layers are not leached free from iron oxide and remain brown.

Of the profiles given in table 8, the first four are in the group under discussion,

but Marikana No. 2 is an intrazonal soil type, black instead of red and falling in the category of glei soils. It occurs only a short distance from the Marikana No. 1 profile and is formed from the same basic igneous rock under the same rainfall; but it occupies a shallow depression, and, instead of good surface drainage, waterlogging is assisted by the surface runoff from surrounding areas. Internal drainage is impeded by the fact that the soil colloid, on wetting, swells and forms

TABLE 9
X-ray results for brown to reddish brown ferruginous lateritic soils

PROFILE AND SAMPLE NO.	DEFINITE	WEAK	DOUBTFUL
Middelwit			
A 8228	Mica, kaolinite		Hematite
A 8230	Mica, kaolinite	Hematite	
A 8232	Mica, kaolinite	Hematite	Montmorillonite
Ventersdorp			
A 8265	Kaolinite, hematite, mica, quartz	Gibbsite	
A 8267	Kaolinite, hematite, mica	Gibbsite, quartz	
A 8269	Kaolinite, hematite, mica	Gibbsite, quartz	
Marikana No. 1			
A 8679	Kaolinite	Hematite	
A 8681	Kaolinite	Hematite, gibbsite	
A 8683	Kaolinite		Hematite, gibbsite
Ermelo			
A 8293	Kaolinite, gibbsite	Hematite	
A 8294	Kaolinite, gibbsite	Hematite	
Marikana No. 2			
A 8686	Montmorillonite, quartz	Kaolinite	
A 8688	Montmorillonite, quartz	Kaolinite	
A 8690	Montmorillonite, quartz	Kaolinite	
A 8692	Montmorillonite, quartz	Kaolinite	

a compact plastic mass which excludes air. On drying, it cracks badly. Under the conditions of its development, it is not leached extensively of soluble constituents and thus differs sharply from all the lateritic types considered in this paper.

Differential thermograms are given in figures 7, 8, 9, and x-ray data are summarized in table 9. The profiles are rather individual in character and require separate discussion.

The Middelwit profile contains a micaceous mineral as the dominant constituent according to x-ray diffraction, and, according to figure 7, this must be identified as illite. In the deepest sample, A 8232, indication of a slight amount of montmorillonite was given by a small, ill-defined peak at about 14 Å. and by a change in shape of the main endothermal peak near 650°C. (fig. 7). High base exchange for the soil, together with low percentages of the clay fractions, was

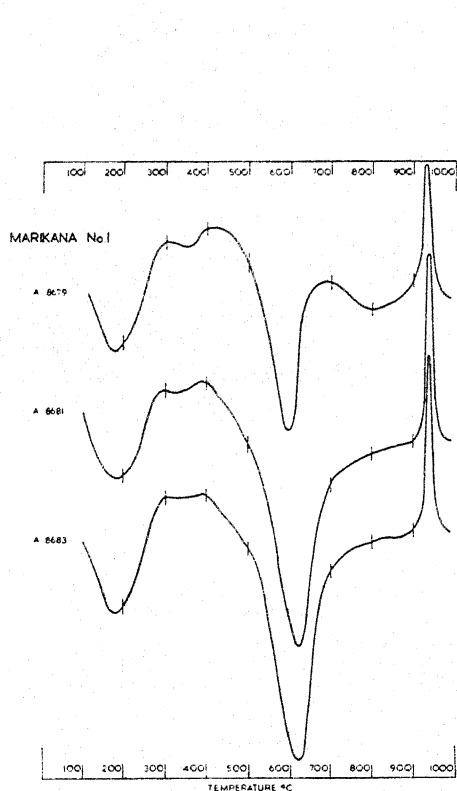


FIG. 8

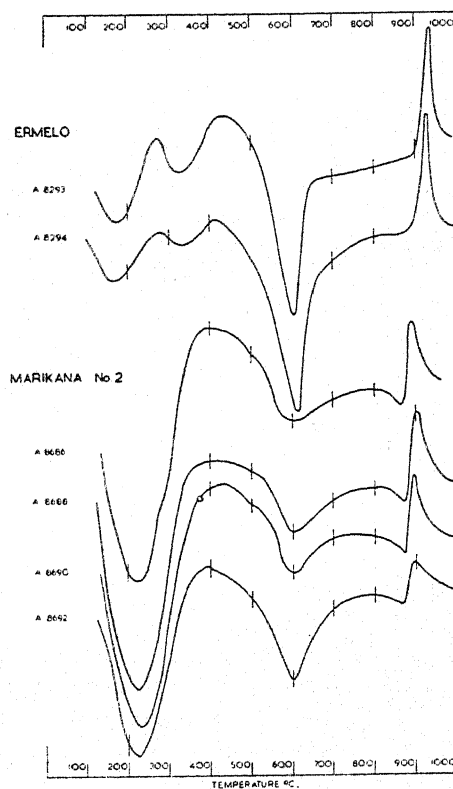


FIG. 9

FIG. 8. DIFFERENTIAL THERMAL CURVES OF BROWN TO REDDISH BROWN FERRUGINOUS LATERITIC SOILS—MARIKANA NO. 1

FIG. 9. DIFFERENTIAL THERMAL CURVES OF BROWN TO REDDISH BROWN FERRUGINOUS LATERITIC SOILS—ERMELO AND MARIKANA NO. 2

in accord with illite or montmorillonite. The nature of the main clay mineral explains why distinct evidence of gibbsite is found, despite the high $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratios.

In the Ventersdorp colloids, mica is much less abundant and is probably present as such, since neither differential thermograms nor base exchange affords evidence of clay minerals other than kaolinite, which is the predominant mineral.

Marikana No. 1 shows a large proportion of kaolinite and no micaceous con-

stituent. In relation to the percentage of the clay fraction, the base exchange is somewhat higher than might be expected for kaolinite alone.

The Ermelo profile is formed under high rainfall conditions and its colloids are similar to those of the red earths, that is, low $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratios, strong evidence of gibbsite, and low base exchange.

The main generalization which seems applicable to the foregoing profiles is that, as rainfall decreases on surfaces with good drainage, weathering is rather to illite than to kaolinite. As it increases, kaolinite tends to decompose to gibbsite, and a change to lateritic earths occurs.

The Marikana No. 2 profile has been formed under conditions of minimum leaching of soluble constituents, and it is hardly surprising, therefore, that it has little in common with the other profiles. Montmorillonite is the predominant mineral, in accord with its high base exchange, its swelling properties, and high $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio. The cause of the black color is not certain, but much of the iron oxide content will be combined in the montmorillonite structure. No iron oxides could be identified by x-ray analysis.

CONCLUSIONS

Pedologists generally contend that soils should be classified entirely on their morphological characteristics. On this basis, the soils under consideration have been classified into five groups. Though doubt may be felt about use of analytical and mineralogical data for the soil or its colloid fraction in classification, it is unquestionably satisfactory to find that such data are in general accord with the morphological classification. In nearly every sample of all the groups, a detectable amount of free alumina, as gibbsite, has appeared in the soil colloids, showing a common tendency for weathering to proceed past the stage of clay mineral formation.

In accord with their close morphological relationship, there are no sharp distinctions between the colloids of laterites, lateritic yellow, and lateritic red earths. When all these are taken together, the most notable feature is a marked dependence of gibbsite content upon rainfall and very little dependence upon parent rock. Their constituents are kaolinite, gibbsite, and iron oxides only. A differentiation might be possible according to the form of the iron oxide, for example, hematite in red earths, goethite in yellow earths, but iron oxides are uniformly so poorly crystallized that their identification is extremely difficult or impossible.

The Bulwer profile is of particular interest, due to presence of illite and complete absence of kaolinite. In this profile, it would appear that gibbsite is obtained directly by weathering of illite, and not through intermediate formation of kaolinite. Of other profiles considered in this paper, the nearest in this respect is Middelwit, in which illite predominates over kaolinite, but the proportion of gibbsite is small, and the presence of some kaolinite gives rise to the possibility that it represents an intermediate stage of decomposition.

In ferruginous lateritic soils, the clay fractions are low and contain considerable proportions of fine quartz and mica, which vary considerably with the parent rock. There is also a tendency for the clay mineral to be illite rather than

kaolinite. Decomposition of the clay minerals is not very intense compared with the other groups.

An intrazonal glei or meadow soil has been included in the discussion, since it shows completely different properties from surrounding soils produced from the same parent rock. These differences are confirmed by its colloid, which constitutes a high proportion of the total soil and consists almost wholly of montmorillonite.

SUMMARY

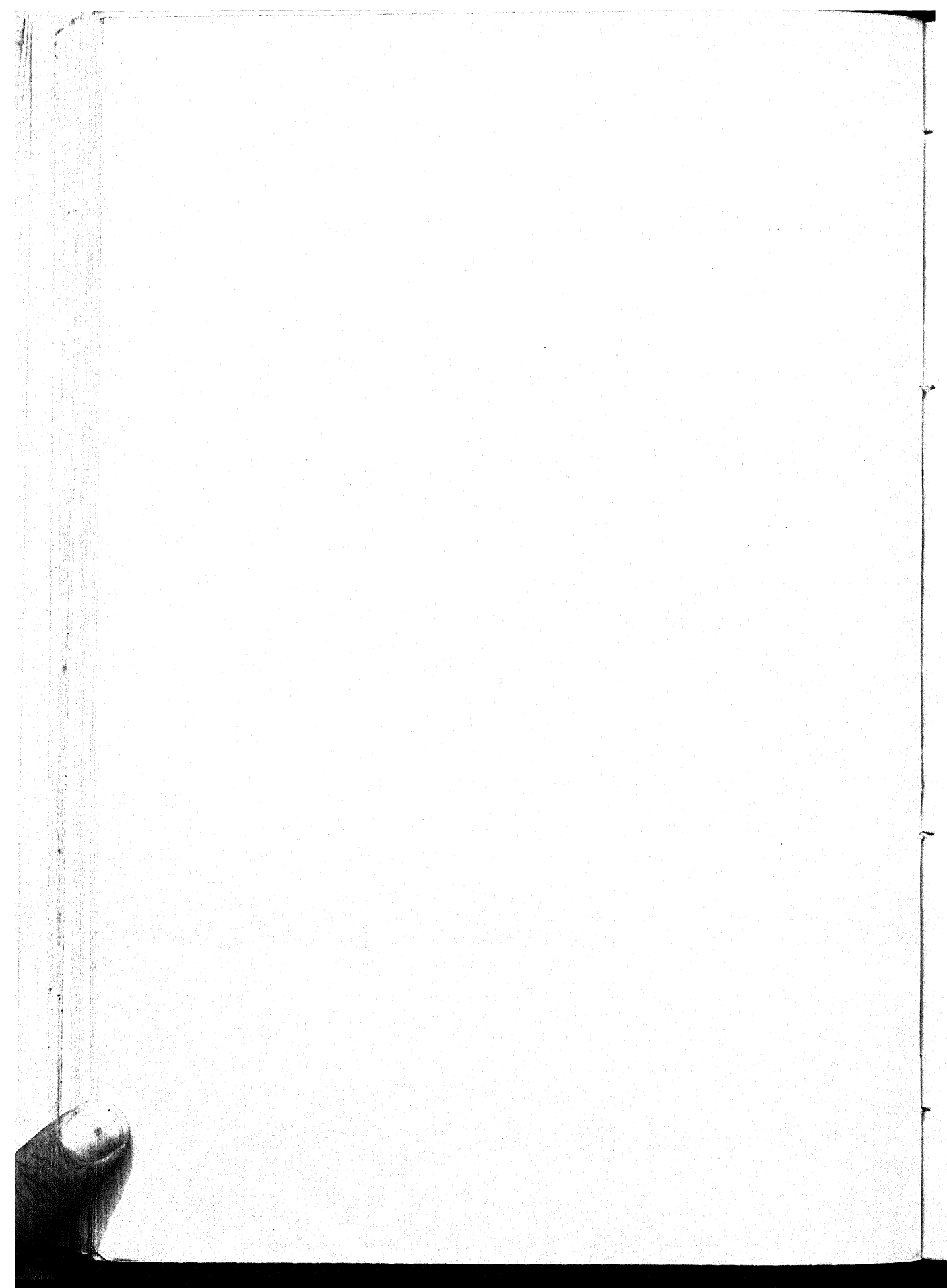
A study has been made of the mineralogical constitution of the colloids of the South African lateritic soils. Chemical analyses were previously reported, and the present work consists of the application of x-ray diffraction and of differential thermal analysis to the same samples.

The results are in general accord with morphological classification of the soils. Under conditions of good drainage and high rainfall, a high degree of weathering takes place, and the soil colloids consist only of kaolinite, gibbsite, and iron oxide. When rainfall is below about 30 inches a year, weathering is less extensive, undecomposed quartz and mica tend to appear in the colloid fraction, and the clay mineral is sometimes illite. Gibbsite, however, continues to appear.

Under conditions of poor drainage, an instance of an intrazonal black soil, with montmorillonite as clay mineral, is cited. In one profile, under conditions of high rainfall and good drainage, there is evidence of decomposition of illite directly to gibbsite.

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BOOKS

Annual Review of Biochemistry. Volume 21. Edited by J. MURRAY LUCK, HUBERT S. LORING, AND GORDON MACKINNEY. Annual Reviews, Inc., Stanford, California, 1952. Pp. 781. Price \$6 plus shipping charges (15 cents in U. S. A., 35 cents elsewhere).

Everyone concerned with plant and animal research will find this volume of much interest and value. The entire set of 21 volumes provides reference material on almost all subjects in these fields. This volume contains review papers by 23 prominent research specialists. These deal with the chemistry of carbohydrates, lipids, steroids, muscle, and nonsteroid hormones; metabolism of fats, amino acids, proteins, and carbohydrates; proteolytic, nonoxidative and nonproteolytic enzymes; fat-soluble and water-soluble vitamins; biochemistry of neoplastic tissue and antibiotics; nucleic acids, purines, and pyrimidines; interrelationships of lipid and carbohydrate metabolism; and nutrition, comparative biochemistry, carotenoids, alkaloids, chromatography, and biological oxidations. Soil-plant specialists will find the discussion of mineral elements in animal nutrition of special interest, and some important references are given. The work of some 6,000 scientists is reviewed. This is a highly important publication.

Chemical Anatomy, Physiology, and Pathology of Extracellular Fluid. Fifth Edition. By JAMES L. GAMBLE. Harvard University Press, Cambridge, Massachusetts, 1951. Pp. 156, charts 52. Price, paper-bound, coil back, \$1.90.

Those who are interested in the mineral nutrient problem in relation to the soil-plant-animal-man cycle will find this book of considerable interest and value. Chart 2, for example, gives comparative analyses of sea water, blood plasma, interstitial fluid, and cell fluid, in terms of acid-base equivalence. In chart 3 one finds that the 155 me. of base in blood plasma consist of 142 me. Na, 5 me. K, 5 me. Ca, and 3 me. Mg, and the acid equivalence consists of 27 me. HCO_3 , 103 me. Cl, 2 me. HPO_4 , 1 me. SO_4 , 6 me. organic acids, and 16 me. protein. The remaining charts show other very interesting relationships. The author is associated with the department of pediatrics, The Harvard Medical School.

Chemistry of the Metal Chelate Compounds. By ARTHUR E. MARTELL AND MELVIN CALVIN. Prentice-Hall, Inc., New York, 1952. Pp. 613. Price \$13.50.

A substance that combines with a metal to form a ring compound is known as a chelating ($\text{ch}=\text{k}$) agent, and the resulting product is a chelate. Interest in this process and in the resulting products has grown rapidly during the last few years, especially in the biological field, particularly in connection with trace-element research. All of the trace elements form chelates with ethylenediaminetetracetic acid, one of the best-known chelating agents. These trace-element chelates vary in their stabilities. Enzymes are chelation systems. Addition of a chelating agent to a biological system may result in very marked changes in the functioning of enzymes, since the agent competes with the enzymes for the

bound metals. These and a great variety of other points are developed in detail in this highly informative and well-written book, which is by far the best presentation of the subject that has come to our attention.

The Diagnosis of Mineral Deficiencies of Plants by Visual Symptoms. By T. WALLACE. His Majesty's Stationery Office, London, British Information Services, New York, 1951. Pp. 108, color plates 311. Price \$8.

The author of this book is director of the Horticultural Research Station at Long Ashton, Bristol. The work reported was done under the sponsorship of the Agricultural Research Council. The five chapters deal with plant nutrition, soil mineral supplies, methods of determining nutrient deficiencies, deficiency symptoms, and visual methods of diagnosis in the field. Extended bibliographies are appended to each chapter. The color plates, the most complete set yet to be published, show deficiency symptoms of all the mineral nutrients known to be required, as they are revealed by potatoes, barley, oats, rye, wheat, maize, flax, broccoli, brussels sprouts, cabbage, savoy, cauliflower, kale, radish, rape, swede, turnip, beets, mangold, spinach, beans, peas, clovers, alfalfa, carrot, parsnip, celery, lettuce, leek, tomato, hop, onion, apple, cherry, pear, plum, currant, gooseberry, raspberry, and strawberry. Every one who has to do with diagnosing soil-plant deficiencies will find this a very valuable book to have close at hand.

The Geography of Hunger. By JOSUÉ DE CASTRO. Little, Brown and Company, New York, 1952. Pp. 337. Price \$4.50.

The question posed by the author of this exceptionally well written book is whether overpopulation is the cause of hunger or hunger is the cause of overpopulation. The point is made that in proportion as the consumption of animal proteins is reduced, the birthrate is increased. This conclusion is supported by a tabulation of birthrates and animal-protein consumption in 17 countries, which, without exception, are shown to be inversely correlated. Thus the birthrate in Formosa is 45.6 and the animal-protein intake per day is 4.7 grams. In Sweden, the birthrate is 15.0 and the animal-protein intake 62.6 grams. The eight chapters in the book deal with taboo and gamut of hunger, hunger in the New World, in Ancient Asia, and in the Dark Continent, starving Europe, advance against hunger, and geography of abundance. If De Castro's concept is correct, population growth can be brought under control by an improved animal-protein diet. The author has presented a highly interesting and constructive statement on this very important subject. The book merits reading by a great many people.

Geography of Living Things. By M. S. ANDERSON. Philosophical Library, New York, 1952. Pp. 202, plates 5. Price \$2.75.

The author of this book endeavors to connect the physical side of geography with the animal and human side in what might be called the science of biogeography. The several chapters deal with man as an animal, effect of environment on man, and his relationships to rocks, water, soil, food, pests, and diseases.

The problem of famine is considered in some detail. The conclusion is drawn that "we have not really solved the famine problem, we have only shelved it. If we let our numbers increase as they are doing at present, when the problem does again present itself for solution in the densely populated urbanized countries of Western Europe and North America, it will be an infinitely more difficult problem than it has ever been hitherto, even in India or China." The author suggests that a true balance between man and the soil would be more easily attained by state ownership of all land, however impalatable that might be.

Guide Pour l'Étude Expérimentale du Sol. Second Edition. By ALBERT DEMOLON AND DESIRÉ LEROUX. Gauthiers-Villars, Paris, 1952. Pp. 251, figs. 88. Price, paper-bound, \$6.05.

This book is recommended for use by students of soils who are endeavoring to improve their reading knowledge of French. It is easy to read and, at the same time, it gives a very good outline of the nature of soil, its chemical, physical, and biological properties, and of methods that are being employed in France in the study of these properties. Methods for determining boron, copper, zinc, nickel, and cobalt are included, and references are given to methods of arsenic, fluorine, iodine, barium, chromium, lithium, molybdenum, lead, rubidium, selenium, titanium, and vanadium determination.

Laterite and Lateritic Soils. By J. A. PRESCOTT AND R. L. PENDLETON. Commonwealth Agricultural Bureaux, Farnham Royal, Bucks, England, 1952. Pp. 51, figs. 7, plates 6. Price 6/-.

The authors give the field characteristics of laterite, its geographical distribution, and its nature and origin, and then consider lateritic soils. They reach the conclusion that "laterite is essentially the exposed illuvial horizon of an ancient soil. The principal difference from a soil in current process of formation is that the scale is very materially greater." They suggest that the term "laterite" as a name for a great soil group be dropped. Kellogg suggests the term "latosol" as a substitute. The photographs and descriptions of laterite in this book are of special interest.

The Mineral Resources of the World. Volume 2. By WILLIAM VAN ROYEN AND OLIVER BOWLES. Prentice-Hall, Inc., New York, 1952. Pp. 181, figs. 186. Price \$10.75.

This second volume of the *Atlas of the World's Resources* is dedicated to the memory of Oliver Edwin Baker, who had a life-long interest in graphic and cartographic presentation. The authors of this volume have made extensive use of these methods in showing the geographic distribution of the world's mineral resources and their points of production. Following a preview, and a discussion of coal, petroleum, and water power, consideration is given to 16 important metals, the uranium group, phosphate rock, potash, sulfur, salt, diamonds, asbestos, fluorspar, graphite, and mica. The world reserves of phosphate rock are estimated to be 26 billion metric tons and those of potash (K_2O) 37

billion metric tons. The United States has about half the phosphate but only about 1 per cent of the potash, enough to last only about 70 years at the current rate of production. This is a highly interesting and attractive volume.

Principles of Agriculture. By W. R. WILLIAMS. Chemical Publishing Co., Inc., New York, 1952. Pp. 156, figs. 34. Price \$3.75.

Translation of this book into English, by G. V. Jacks, and of T. D. Lysenko's introduction, by Bernard L. Koten, makes it possible to get an idea of current Russian thinking on soils in relation to crop production. The point of primary concern is soil structure and the means by which it can be improved, both by proper use of implements for cultivation and by the growing of perennial grasses. The author writes: "Cultivation must produce a crumb structure throughout the whole arable horizon, but in such a way that the smallest possible quantity of dispersed soil particles is created at the same time." He also indicates that two years of a perennial grass are required for complete restoration of a soil of which the structure has been completely destroyed. Another point of interest is the concept that potassium fertilizers should be applied to the sod crop rather than to cultivated crops, as a means of avoiding deterioration of soil structure. Lysenko's introduction advises the reader as to how much of Williams' thinking is sound and as to what must be discarded.

Proceedings of the Bihar Academy of Agricultural Sciences. Volume 1, Number 1. Agricultural Research Institute, Sabour (Bihar), India, January, 1952. Pp. 94. Annual subscription Rs. 10.

Three numbers of these proceedings will be published annually. This first number contains seven papers having to do with hybridization in *Luffa acutangula*; exchange cations in soils; size and shape of wheat plots; fruit-producing population of papaya; cytological studies in *Loranthus*; carbon dioxide production in stored wheat; and soils of Bihar, with new method for determining manurial requirements. A number of the articles are illustrated, and a considerable list of references is appended to each of them. The secretary-treasurer of the editorial board is S. C. Mandal.

Punched Cards, Their Applications to Science and Industry. Edited by ROBERT S. CASEY AND JAMES W. PERRY. Reinhold Publishing Corporation, New York, 1951. Pp. 506. Price \$10.

This is the first carefully developed and detailed discussion of this subject that has come to our attention. The book is divided into four parts having to do with fundamentals, case histories, general considerations, and future possibilities. The authors are well known men in their respective fields in industry, the universities, and the societies. The point is made that publication has extended far beyond our ability to make use of it unless the principle of the punched-card is applied to the problem. The book is intended primarily to help the individual scientist or technologist, with more emphasis on hand-sorted than machine-sorted cards. The cards are especially useful in working with problems that in-

volve large groups of data, such as those dealt with by D. E. H. Frear in his book on chemical structure in relation to toxicity of compounds to insects and fungi. A highly important chapter on indexing and index-searching was written by E. J. Crane, editor of *Chemical Abstracts*. It would appear that more attention should be given to the punched-card system, particularly by individuals. A bibliography of 276 references is appended. This is an important book.

The Reports of the Institute of Agricultural Research. Volume 3. Series D Agriculture. Tohoku University, Sendai, Japan, 1951. Pp. 171.

Of the seven papers in this issue, those on "mechanisms of phosphorus and iron absorption by rice plant" and on "a newly devised method for soil colloidal fractionation" in which thermal diffusion is applied would be of particular interest to soil-plant scientists.

Rothamsted Experimental Station Report for 1951. Harpenden, England, 1952. Pp. 212. Price, paper-bound, 7/6, plus foreign postage.

As in previous issues, this report gives a short history of Rothamsted, lists the staff members, and then presents the reports of the 15 departments. In addition, it reports progress on the soil survey of England and Wales. It also has special reviews on yellow virus of beets, manganese oxidation in higher plants, and travel distances of insects. Titles and authors are given for 140 technical papers that were published during the year. The frontispiece shows a picture of the Rothamsted laboratories and the last page contains a map of the experimental farm. Anyone who has to do with agriculture will find something of interest and importance in this report.

Soluble Silicates. Volume 1. By JAMES G. VAIL. Reinhold Publishing Corporation, New York, 1952. Pp. 357. Price \$9.

This is the first of a two-volume monograph designed to present a complete review of the known properties and industrial applications of soluble silicates. It is sponsored by the American Chemical Society. Following an introductory historical chapter, the author discusses present practices in silicate manufacture and homogeneous, heterogeneous, and complex systems. Soil chemists will find the entire volume of much interest. For those concerned with soils in relation to plant nutrition, there is an excellent review of the literature on silicon as a possible plant nutrient and nutrient replacement. Some consideration is given to silicates as soil-aggregating agents. References are given to the work of more than 1,000 research specialists in silicate chemistry and practice. Every soils department will want a copy of this volume for ready reference.

A Source Book in Chemistry. Edited by HENRY M. LEICESTER AND HERBERT S. KLINKSTEIN. McGraw-Hill Book Company, New York, 1952. Pp. 554. Price \$7.50.

This is the seventh of a series of source books on astronomy, mathematics, physics, geology, Greek science, animal biology, and chemistry. Comments

concerning and selected quotations from 83 noted chemists are presented, beginning with Biringuccio (1480-1539), Agricola, Paracelsus, Libravius, and Van Helmont; later including Ingenhous, Lavoisier, Davy, Wöhler, Liebig, and Pasteur; and ending with Fischer, Büchner, Thiele, Gomberg, Werner, and Marie Curie (1867-1934). The selections are made on the basis of showing the gradual development of chemical theory. A bibliography of biographies of nearly 400 titles is appended. In following the development of the text, one soon becomes aware that although the facts of chemistry are fixed this does not apply to the theories that were advanced to explain them. Yet the theories have been much more productive than mere knowledge of the facts on which they were based. This is an inspiring volume that students of chemistry would do well to read early in their careers.

Viruses as Causative Agents in Cancer. C. R. RHOADS, Consulting Editor. Annals of the New York Academy of Sciences, volume 54, pp. 869-1232. Published by the Academy, New York, 1952. Price \$4.

This consists of a series of papers that were presented at a conference on viruses as causative agents in cancer held by the Section of Biology of the New York Academy of Sciences, November 16-17, 1951. The consulting editor is director of Sloan-Kettering Institute for Cancer Research and director, Memorial Center for Cancer and Allied Diseases, New York. Of the three hypotheses—irritation, embryonal, and parasitic—only the last is dealt with. The 31 technical papers present highly important information on pathology, cell particulates, enzymes, biochemical relationships, proliferation, genetic factors, immunological barriers, dormancy, lymphomatosis, isolation, tumors and virus in mice, fowl, plant, fish, frog, and rabbit, crown-gall disease, Hodgkin's disease, mouse leukemia, electron microscopy of viruses, and virus-induced tumors of human skin. The editor points out that "knowledge of cell particulates and the neoplastic process has increased enormously" in the last 40 years and that new information on the "cancer problems has never been acquired so rapidly nor has it been of such high quality." This is a very valuable issue of the Annals.

THE EDITORS

SOIL SCIENCE

VOLUME 74

December 1952

NUMBER 6

AVAILABILITY OF RESIDUAL PHOSPHORUS OF SUPERPHOSPHATE AND ROCK PHOSPHATE DETERMINED BY PHOSPHORUS IN CROPS FROM RADIOACTIVE SUPERPHOSPHATE¹

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Received for publication March 19, 1952

Many of the soils of western Florida are known to have the capacity to fix large amounts of the phosphorus of applied phosphate fertilizers.³ In their virgin state these soils require addition of phosphates as well as other fertilizing elements to ensure a crop of economic value. Thus the response of white clover and Dallis grass, planted on virgin Tifton and Carnegie fine sandy loams, was a straight-line function of increasing amounts of superphosphate up to 1,000 pounds per acre (2).

As only a small part of the phosphorus added to these soils is recovered in crops, the soil will, after a period of fertilizing and cropping, accumulate a considerable supply of residual phosphorus. The question arises: How available is this phosphorus to succeeding crops? If the amount is known to be considerable, a farmer might find it worth while to supply not only adequate phosphorus for the current crop but some reserve also, particularly of the cheaper but more insoluble phosphates.

The advent of radioactive phosphorus in quantities adequate and cheap enough for the tagging of fertilizer phosphates for field experiments makes it possible to determine how much of the phosphorus in the crop comes from currently applied phosphate. The remainder of the plant phosphorus can be credited to the residual supplies in the soil, except for the phosphorus that may enter into an exchange with that native to the soil. This native phosphorus is probably negligible for Marlboro fine sandy loam of approximately 200 ppm. phosphorus, which constituted the plot area of this experiment. This is the procedure reported in this paper for a soil characterized by a high fixing power for phosphorus and to which phosphates must be added for satisfactory growth of crops.

EXPERIMENTAL

A series of plots, 5 by 20 feet, were laid out in quadruplicated randomized block design in a field of Marlboro fine sandy loam. The field was first cropped in 1947

¹ The radiophosphorus was supplied by the Atomic Energy Commission and incorporated into superphosphate by the Bureau of Plant Industry, Soils, and Agricultural Engineering, Beltsville, Maryland.

² Journal Series 62. The authors express their appreciation for aid and interest in these experiments to R. W. Pearson, C. E. Hutton, W. H. Kelly, and W. K. Robertson. Some of the earlier assays for P^{32} were made under the direction of J. W. Borland.

³ From unpublished data by Neller and in Reference (4).

and had received applications of superphosphate totaling 116 pounds per acre, P_2O_5 basis. In August 1949 ground limestone at 1,000 pounds per acre was disked into the surface 6 inches. A month later superphosphate (18 per cent P_2O_5) and

TABLE 1
Phosphorus in oats and fescue obtained from residual phosphates of previously applied superphosphate and rock phosphate on Marlboro fine sandy loam

1950				1951			
Pretreatments of phosphate Aug. 23, 1949	Tagged super- phosphate Nov. 11, 1949	P in oats obtained from residual phosphates		Residual phosphate*	Super- phosphate of Mar. 14, 1951†	P in fescue obtained from residual phosphates	
		1st cutting Jan. 5, 1950	2nd cutting Feb. 14, 1950			1st cutting May 1, 1951	2nd cutting June 1, 1951
lb.‡/A.	lb.‡/A.	%	%	lb.‡/A.	lb.‡/A.	%	%
100 (superphosphate)	100	43.8	46.2	200	50	—	—
	200	32.3	30.1	300	100	58.6	64.5
	300	24.8	23.8	400	150	48.0	50.9
200 (superphosphate)	100	57.6	57.6	300	50	73.9	78.4
	200	48.3	41.3	400	100	58.1	60.1
	300	43.2	32.7	500	150	52.6	50.9
300 (superphosphate)	100	68.3	61.2	400	50	73.5	75.7
	200	56.0	53.1	500	100	62.5	68.9
	300	49.9	39.7	600	150	—	—
320 (rock phosphate)	100	23.4	35.4	420	100	53.7	56.8
640 (rock phosphate)	100	36.2	44.3	740	100	56.1	57.2
L.S.D. re pretreatments of superphosphate		3.9	5.7			—	—
L.S.D. re 100 P_2O_5 -tagged superphosphate treat- ments		4.5	10.0			§	4.8

* All plots received 116 pounds P_2O_5 as superphosphate applied to the virgin soil in 1947 and 1948.

† The superphosphate of the 100 P_2O_5 rate was radioactive.

‡ P_2O_5 .

§ Not significant.

rock phosphate were disked into the surface 4 inches of the plots at rates recorded in table 1.

Three months later, radioactive superphosphate of an activity of 0.2 mc. per gram of phosphorus was applied in drills 7 inches apart, just below the soil sur-

face.⁴ The plots were planted to fescue grass after adequate amounts of nitrate and potash were added.

Extremely dry weather killed the fescue grass, and the area was planted to oats on November 30, and equipment was installed to irrigate the plots when necessary. On January 5 a cutting of oats was removed. Samples were taken for yield and for assay by the method of MacKenzie and Dean (3). After the removal of a second cutting, the plot area was topdressed with nitrate and potash and planted to fescue in preparation for the experiments of 1951. For these the current applications of superphosphate were at rates of 50, 100, and 150 pounds P_2O_5 per acre, of which the 100-pound rate was tagged with P 32.

Inasmuch as crops are a failure on Marlboro fine sandy loam in its virgin state unless a phosphate is added to the soil (2), the phosphorus in the plant that was not derived from the currently supplied superphosphate can be assumed to come from the residual phosphorus in the soil and is so recorded.

Differences necessary for significance (L.S.D.) in the tables are calculated at the 5 per cent level of probability.

RESULTS

Table 1 records the percentage phosphorus in the oats obtained from the residual or pretreatment phosphorus of superphosphate and rock phosphate in 1949. In both first and second cuttings of 1950 more than 40 per cent of the phosphorus in the oats was derived from residual phosphates where the current applications of superphosphate were at the rate of 100 pounds P_2O_5 per acre. Increasing the rate of application lowered the amount of phosphorus coming from residual phosphates to about 24 per cent of the total uptake. Larger amounts of pretreatment (residual) superphosphate were paralleled by a higher percentage uptake of phosphorus from the residual phosphates.

The data of 1950 (table 1) definitely show that there was more phosphorus in the oats from residual superphosphate where more had been applied to the soil in the pretreatments. The increases were significant for all three pretreatment levels.

Two of the currently applied superphosphate treatments at the rate of 100 pounds per acre followed pretreatments of rock phosphate at two rates. The uptake of phosphorus from these differed significantly for the first cutting (table 1), and that for the 640-pound P_2O_5 per acre rate amounted to 44.3 per cent. The uptake of phosphorus from rock phosphate at the rate of 1 ton per acre (640 pounds P_2O_5) was about the same as from 100 pounds P_2O_5 applied in superphosphate.

The 1951 treatments of superphosphate were at rates of 50, 100, and 150 pounds P_2O_5 per acre (table 1). Superphosphate at the 100-pound rate was tagged, and uptake of phosphorus for the other rates was calculated by means of the A value formula (1). The blank spaces in the table are due to impossibility of calculation because there is no tagged rate with a similar background, as shown in the

⁴ The radiosuperphosphate was applied by means of a machine designed and built by J. G. Futral, Georgia Agricultural Experiment Station, aided by funds from the Phosphate Industry Committee.

column of residual phosphates for 1951. For this reason also, significant differences could not be calculated for residual effects of superphosphate of the pre-treatments.

TABLE 2

Yields and phosphorus content of oats and fescue relative to applications of superphosphate and rock phosphate on Marlboro fine sandy loam

Yields and treatments on acre basis

1950						1951					
Pretreatments of phosphate Aug. 23, 1949	Tagged super- phosphate Nov. 11, 1949	Oats				Residual phos- phate* lb.‡/A.	Super- phosphate of Mar. 14, 1951 lb.‡/A.	Fescue			
		1st cutting Jan 5, 1950		2nd cutting Feb. 14, 1950				1st cutting May 1, 1951		2nd cutting June 1, 1951	
		Yield†	P con- tent	Yield†	P con- tent			Yield†	P con- tent	Yield†	P con- tent
lb.‡/A.	lb.‡/A.	lb.	%	lb.	%			lb.	%	lb.	%
100 (superphosphate)	100	165	.316	215	.258	200	50	1127	.299	161	.231
	200	229	.412	445	.300	300	100	1352	.355	157	.245
	300	195	.434	300	.297	400	150	1106	.343	122	.280
200 (superphosphate)	100	214	.389	217	.278	300	50	1311	.315	148	.255
	200	205	.398	299	.304	400	100	1220	.364	170	.260
	300	213	.439	377	.317	500	150	1383	.325	157	.292
300 (superphosphate)	100	244	.414	266	.303	400	50	1301	.294	151	.256
	200	204	.459	362	.307	500	100	1167	.377	148	.267
	300	261	.432	423	.247	600	150	1301	.323	155	.266
320 (rock phosphate)	100	189	.328	311	.260	420	100	1337	.337	137	.224
640 (rock phosphate)	100	163	.351	145	.017	740	100	1227	.348	145	.231
L.S.D. re pre- treatments of superphosphate		§	.022	90	.025			§	.024	§	.020
L.S.D. re 100 P ₂ O ₅ -tagged superphosphate treatments		§	.038	§				§	.041	§	.035

* All plots received 116 pounds of P₂O₅ as superphosphate applied to the virgin soil in 1947 and 1948.

† Air-dry basis.

‡ P₂O₅.

§ Not significant.

Differences in phosphorus uptake with superphosphate currently applied at 100 pounds per acre P₂O₅ were not significant for the first cutting but were for the second (table 1), particularly in a comparison of residual effects of superphosphate

and of rock phosphate. In 1951, as in 1950, it may be observed that the residual effect of 2,000 pounds of rock phosphate (32 per cent P_2O_5) was about equal to one fourth that amount of 20 per cent superphosphate.

Yield data of oats in 1950 and of fescue in 1951 for these plots are recorded in table 2. Yields increased with increased phosphates applied to the soil, but not significantly except for the second cutting in 1950. Plots without a pretreatment of phosphate were not included in this experiment, because it was known that

TABLE 3

Total and dilute-acid-soluble phosphorus content and pH of surface 3 inches of Marlboro fine sandy loam of phosphated plots

PRETREATMENTS OF PHOSPHATE AUG. 23, 1949	SUPERPHOSPHATE NOV. 11, 1949	TOTAL P JAN. 5, 1950	DILUTE- H_2SO_4 - SOLUBLE P JAN. 5, 1950	pH MAY 1, 1951
<i>lb.* / A.</i>	<i>lb.* / A.</i>	<i>ppm.</i>	<i>ppm.</i>	
100	100	263	55	6.08
(superphosphate)	200	319	66	6.00
	300	271	50	5.77
200	100	375	79	6.08
(superphosphate)	200	318	58	5.98
	300	458	87	5.77
300	100	386	74	6.26
(superphosphate)	200	435	78	6.10
	300	400	91	5.94
320	100	399	108	6.26
(rock phosphate)				
640	100	673	245	6.12
(rock phosphate)				
L.S.D. re pretreatments, super- phosphate		6	0.6	0.16
L.S.D. re superphosphate treatments of Nov. 11, 1949		30	3.2	0.27

* P_2O_5 .

establishment of a crop preceding the addition of tagged superphosphate would be doubtful without an initial treatment of phosphate.

Table 2 also records the phosphorus content of the oats in 1950 and of the fescue in 1951. The percentage of phosphorus in the plants was significantly increased where larger amounts of phosphates had been applied currently and where the residual levels were higher. Only 0.89 per cent of the phosphorus of the phosphates added to the soil was taken up by the oats grown in 1950, and 2.28 per cent by the fescue of the two cuttings recorded for 1951. Recovery from the

rock phosphate treatments averaged 0.50 per cent in 1950 and 1.68 per cent in 1951.

There is a significant trend toward more total phosphorus in the surface 3 inches of the Marlboro soil (table 3) with increasing rates of application of superphosphate. The increase is not consistent, however. This is not surprising in view of the high dilution factor resulting from mixing the superphosphate in the surface 3 inches of this soil, which in virgin state contains about 200 ppm. of phosphorus. About one fifth of the total phosphorus was extracted with the 0.002 N H_2SO_4 buffered solution, with significance in most cases in reference to the amounts of superphosphate added to the soil. An increase in the amount of rock phosphate had a marked effect on both total and soluble soil phosphorus but not on percentage phosphorus in the oats and fescue (table 2), whereas an increase in the amount of superphosphate resulted in significant increases in plant phosphorus.

The pH values of the soil in samples taken in May 1951 (table 3) were increased slightly but significantly in plots that received pretreatments of superphosphate (300-pound P_2O_5 basis) in September 1949; whereas there was a significant decrease in pH following superphosphate at the 300-pound P_2O_5 rate applied as a topdressing in November 1949 and at the 150-pound rate in March 1951, as compared with applications at one third those rates.

DISCUSSION

The Marlboro soil on which these experiments were run contains practically no soil phosphorus that is available to crops. This factor makes it possible to credit phosphorus uptake by crops to pretreatment or residual applications of fertilizer phosphate after deducting the uptake from currently applied superphosphate. The soil had been cropped for 2 years before establishment of the experimental crops. During that time superphosphate equivalent to 116 pounds P_2O_5 had been applied to the soil. Since this is a negligible amount to add to virgin soils of that type (2), virtually all of the uptake from residual phosphorus can be attributed to the pretreatments of phosphate applied in setting up the experiment. The amounts of phosphorus obtained from pretreatment or residual phosphorus ranged from 43.8 to 66.3 per cent (table 1) when tagged superphosphate was used at the rate of 100 pounds P_2O_5 per acre. This availability of residual phosphorus seems surprisingly high and might be attributed to incomplete fixation equilibrium, were it not for the fact that the uptake from similar amounts of residual phosphorus the next year was fully as high.

Data of 1950 and 1951 show that uptake of phosphorus from rock phosphate was about the same as that from one fourth as much superphosphate. The soil had been limed moderately and had a pH of 6. The results indicate that rock phosphate applied at 2 or 3 tons per acre would serve as a source of phosphorus for pastures on soils of this type. Experiments have shown, however, that over much of Florida, soils need to be supplied with a source of sulfur (5) as well as with phosphorus for satisfactory growth of legumes. Ordinary superphosphate contains sulfur as gypsum.

SUMMARY AND CONCLUSIONS

The availability of the phosphorus of pretreatments of superphosphate and of rock phosphate disked into the surface 4 inches of Marlboro fine sandy loam was determined by addition of radioactive superphosphate to plots in a randomized block design.

More than 40 per cent of the phosphorus in a crop of oats was obtained from the residual phosphorus of superphosphate applied at 100 pounds P_2O_5 per acre. Pretreatments at 300 pounds per acre resulted in more than 60 per cent uptake of phosphorus from residual phosphates.

Use of tagged superphosphate for a second year on the same plots, where a sodded stand of fescue grass had been established, showed that about 60 per cent of the phosphorus in the grass came from phosphate residual in the soil to the extent of 300 pounds P_2O_5 per acre. On plots that carried 500 pounds, the uptake from the residual source was about 65 per cent.

For oats in 1950 and for fescue in 1951, the uptake from the residuals of finely ground rock phosphate at 640 pounds P_2O_5 per acre was equal to that from superphosphate at 100 pounds P_2O_5 per acre. Use of rock phosphate resulted in decreases in yields and in percentage phosphorus in the crops, as compared with superphosphate.

Total phosphorus as well as buffered dilute- H_2SO_4 -soluble phosphorus of the soil gave poor correlation with the availability of the residual phosphorus as determined by means of radiophosphorus. The soils from the plots of the various treatments ranged in pH somewhat above and below 6.0, with a significant decrease in pH paralleling increased amounts of superphosphate surface dressed on the plots about 6 weeks in advance of the sampling of the soil.

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UTILIZATION OF THE PHOSPHORUS OF ALGAL CELLS AS MEASURED BY THE NEUBAUER TECHNIQUE

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Received for publication January 16, 1952

Most of the cultivated soils in Arizona are favored by extended periods of warm weather and receive water by means of irrigation. These conditions permit rapid growth of soil algae. Observations of undisturbed irrigated soils reveal the presence of a covering of green algae throughout most of the year. Irrigation ditches are also lined with algae. Observations of this nature in addition to counts made by the dilution method leave little doubt that irrigated soils are well supplied with algae. A report by Fletcher and Martin (6) indicates not only the abundance of algae in desert soils but also the importance of these plants in the nitrogen economy because of their ability to fix atmospheric nitrogen. An increase of as much as 3 tons of carbon per acre 3-inch slice, or 1,000,000 pounds of soil, has been attributed by Fletcher² to growth of algae during favorable weather conditions in Arizona. This represents about 6 tons of organic matter, since algae contain between 40 and 50 per cent carbon. Lesser quantities, however, are more common.

Immediately after soils receive water, algae appear to multiply rapidly. At this time they may be expected to fix or immobilize plant nutrients such as phosphorus. As the soils become dry, algal activity decreases, the algae die, and during the process of decay, nutrients are returned to the soil for plant use.

The release of nutrients from algal material by decay is reported here. By use of radiophosphorus the uptake of phosphorus by barley seedlings from algal material and liquid H_3PO_4 added to various calcareous soils was investigated under conditions of the Neubauer technique.

METHODS AND MATERIALS

Preparation of labeled algae

Gallon glass jars containing phosphate-free Bristol's NaNO_3 solution (4) were inoculated with a culture of the green alga, *Palmela* of the Chlorophyta division, and allowed to incubate in the sunlight for 2 weeks. This alga is found abundantly in Arizona soils and was isolated from a citrus-orchard soil. Radiophosphorus in the form of KH_2PO_4 was added at the rate of 1 gm. per 60 liters of solution. The activity of this amount of irradiated KH_2PO_4 was calculated to be about 10 mc. at the time of its addition. The phosphorus concentration of the nutrient solution was brought up to the requirement of the Bristol's medium with an additional 11 gm. of KH_2PO_4 . After incubation in the greenhouse for 34 days the algae were

¹ Cooperative project between the University of Arizona and U. S. Atomic Energy Commission under research contract No. AT (11-1)-103.

² Unpublished data.

concentrated by centrifuging, washed three times with distilled water and three times with 0.002 N H_3PO_4 solution. A final washing was made with distilled water until the washings were free from traces of phosphorus. A suspension of known concentration of the algae was prepared by stirring in a Waring blender for 10 minutes and making up to a volume of 1 liter. Dry-weight determinations were made on 10-ml. aliquots. The 60 liters of culture yielded about 15 gm. of oven-dry algae. A duplicate culture later prepared in the foregoing manner gave somewhat higher yields of algae. The composition of the two algal materials is given in table 1.

Preparation of radioactive phosphoric acid solution

Irradiated KH_2PO_4 was dissolved in 85 per cent H_3PO_4 in a concentration to give specific activity similar to that of the algae. The concentration of phosphorus in the H_3PO_4 solution was also made the same as that of the algal suspensions.

TABLE 1
Carbon, nitrogen, and phosphorus content of algae and extracted oat straw

MATERIAL	CARBON	NITROGEN	TOTAL PHOSPHORUS	C/N	C/P
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		
Algae*	40.1	3.86	3.292	10	12.1
Algae†	40.0	3.94	8.751	10	4.6
Extracted oat straw	43.6	0.175	0.008	249	5450.0

* Used in first Neubauer experiment.

† Used in study of rate of utilization.

Preparation of extracted oat straw

Mature oat straw was ground to pass a 40-mesh screen and treated in a partly opened autoclave in flowing stream for 4 hours with 1 per cent NaOH. The alkali was removed by washing alternately with dilute H_2SO_4 and water over broad-cloth. Table 1 shows some chemical characteristics of the extracted oat straw.

Neubauer technique

Preliminary experiments. A modified Neubauer technique as outlined by McGeorge (11) was employed in the preliminary study designed to compare the availability of algal material with that of liquid H_3PO_4 fertilizer. The pertinent points in the modified Neubauer method are: (a) 100-gm. samples of soil are mixed with 50 gm. of silica sand and the desired phosphorus treatments; (b) the treated soils are placed in Neubauer dishes on the surface of 100 gm. of silica sand and covered with 50 gm. of sand; (c) Arivat barley (100 seeds) is uniformly placed on the sand and covered with an additional 150 gm. of sand; (d) the soil-sand culture is brought up to a previously determined optimum moisture content and maintained throughout the 15-day period of culturing; (e) both tops and roots are harvested for analysis 15 days after seeding.

The soils used, Pima clay loam (virgin) and McClellan clay loam (virgin and

cultivated), were selected for their wide variation in levels of available phosphorus and total organic matter content. These soils, the chemical characteristics of which are shown in table 2, were used throughout the investigations. Treatments

TABLE 2
Analytical data on soils used in the Neubauer experiments

SOIL TYPE	DEPTH	pH	NITROGEN	PHOSPHATE			ORGANIC CARBON	CaCO ₃	C/N
				Total	Or-ganic	CO ₂ -soluble			
	<i>inch</i>		<i>per cent</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>per cent</i>	<i>per cent</i>	
Pima clay loam (virgin).....	0-6	8.1	0.213	1580	760	13.00	2.50	0.16	8.5
McClellan clay loam (virgin).	0-6	8.1	0.0901	995	279	1.44	0.74	6.25	8.2
McClellan clay loam (cultivated).....	0-6	8.0	0.0576	390	85	0.70	0.46	0.37	8.0

TABLE 3
Treatments used in the Neubauer experiments
Per-acre basis

TREATMENT	ALGAE	EX-TRACTED OAT STRAW	PHOSPHORUS AS P ₂ O ₅		NITROGEN AS N		C/N*	C/P*
			From algae	From H ₃ PO ₄	From algae	From urea		
	<i>ton</i>	<i>ton</i>	<i>lb.</i>	<i>lb.</i>	<i>lb.</i>	<i>lb.</i>		
1. Algae.....	1	—	150	—	77.2	—	10	12
2. Algae.....	2	—	300	—	154.4	—	10	12
3. Algae.....	4	—	600	—	308.8	—	10	12
4. Algae, Extracted oat straw.....	2	2	300	—	154.4	—	22	26
5. Algae, extracted oat straw, urea†.....	2	2	300	—	154.4	76.5	15	26
6. H ₃ PO ₄	—	—	—	150	—	—	—	—
7. H ₃ PO ₄	—	—	—	300	—	—	—	—
8. H ₃ PO ₄	—	—	—	600	—	—	—	—
9. H ₃ PO ₄ , extracted oat straw.....	—	2	—	300	3.5‡	—	249	13
10. H ₃ PO ₄ , extracted oat straw, N†.....	—	2	—	300	3.5‡	76.5	22	13
11. Silica sand, algae....	1	—	150	—	77.2	—	10	12
12. Silica sand, algae....	½	—	75	—	38.6	—	10	12
13. Soil alone.....	—	—	—	—	—	—	—	—

* C/N and C/P of treatment materials.

† Nitrogen added to bring total of the straw up to 2.00 per cent.

‡ From straw.

for this study are given in table 3. Each treatment was replicated three times for each soil.

Rate of availability of algal phosphorus. A second study was designed to follow the rate of uptake of algal phosphorus from soil during the first 35 days of contact.

The modified Neubauer technique was also employed in this investigation, though the method of treatment application had to be altered somewhat. The treatments consisting of algal material and liquid H_3PO_4 had to be small enough to allow for as complete mineralization as possible in the 35-day period selected, and still be large enough to allow measurement of the P 32 activity. Applications of 200 pounds of P_2O_5 per acre were thought to meet this objective. Two replications of each treatment were made. One series was treated by injecting the algal suspension into the soil with a pipette. A second series was treated similarly with liquid H_3PO_4 at the same rate of P_2O_5 per acre. Four injections were made in widely separated positions. The cultures were allowed to incubate for various periods ranging from 0 to 20 days at an optimum moisture level before barley was seeded. The plants were harvested in 15 days. This allowed the elapsed time to range from 15 to 35 days during which the treatments were in contact with the soil. Additional Neubauer cultures were prepared, immediately seeded to barley, and given treatments of algal material and liquid H_3PO_4 at intervals during the growth of the seedlings to permit the phosphate sources to be in contact with the soil for various periods ranging from 1 to 15 days. These treatments, too, were harvested 15 days after the seedlings were planted.

The effect of soil microorganisms on the rate of utilization of phosphorus from the algal material and liquid H_3PO_4 was determined by comparing the phosphorus uptake by barley seedlings in sterilized Neubauer cultures with those in the unsterilized cultures described. The sterilized cultures were prepared and heated in an autoclave at 15 pounds' pressure for 2 hours. Before being seeded with sterilized barley, the cultures were allowed to stand for 1 day. The algal material used in all cultures to determine the rate of availability was sterilized in an autoclave for 1 hour at 10 pounds' pressure.

Chemical methods

Total phosphorus of the biological materials was determined by the molybdi-vanado-phosphoric acid method (10). Carbon analysis of the biological materials was made by wet oxidation (1). Nitrogen was analyzed by the mikrokjeldahl method. Inorganic phosphorus of the algae was determined according to the method of Pons and Guthrie (14); that of the soils, by the method of Dickman and Bray (5). Measurement of P 32 and P 31 of the algae and plant materials was made by the procedure of MacKenzie and Dean (12). Organic phosphorus of the soils was determined by the method of Pearson (13).

RESULTS AND DISCUSSION

Preliminary Neubauer experiments

The limited amount of algal material that could be produced by available cultural means made it necessary to depend on the Neubauer method for studying the availability of this material to plants. Although the results obtained may not always be interpreted as identical with those in the field, Neubauer data are useful for predicting the relative value of treatments under field conditions. Moreover, the potential availability of the algal phosphorus compared with that of liquid

H_3PO_4 in different soils is thought to be revealed more accurately under the controlled conditions of the Neubauer method than under uncontrolled conditions in the field.

The preliminary Neubauer experiments were designed to compare the utilization of phosphorus of algal material with that of a wholly soluble source, liquid H_3PO_4 . Dry weight, total phosphorus, and phosphorus absorbed from the treatments were determined on the combined barley tops and roots.

Dry weight of plant. At the end of 15 days there were no significant differences in the dry weights of the barley seedlings attributable either to source of phosphorus or rate of application (table 4). Wide differences in C/N of the extracted

TABLE 4

*Dry weight, total phosphorus, and uptake of phosphorus from algae and liquid H_3PO_4 by barley seedlings grown under conditions of the Neubauer technique**

TREATMENT†	DRY WEIGHT				TOTAL PHOSPHORUS				PHOSPHORUS UPTAKE							
									From soil‡				From Treatment			
	P§	Mv	Mc	s	P	Mv	Mc	s	P	Mv	Mc	s	P	Mv	Mc	s
	gm.	gm.	gm.	gm.	%	%	%	%	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
1	2.44	2.31	2.24	—	0.796	0.613	0.621	—	5.9	1.1	0.6	—	2.5	2.1	2.3	—
2	2.47	2.33	2.24	—	0.831	0.696	0.690	—	5.4	1.0	0.6	—	4.1	4.2	3.9	—
3	2.42	2.36	2.17	—	0.833	0.766	0.794	—	3.8	0.5	0.2	—	5.4	6.6	6.0	—
4	2.39	2.35	2.15	—	0.813	0.644	0.712	—	4.5	0.5	0.6	—	3.9	3.6	3.7	—
5	2.43	2.35	2.19	—	0.861	0.693	0.714	—	5.9	0.4	0.7	—	4.8	3.6	3.9	—
6	2.41	2.50	2.28	—	0.829	0.568	0.601	—	7.2	1.8	0.7	—	1.8	1.4	2.0	—
7	2.44	2.45	2.31	—	0.824	0.670	0.661	—	5.8	2.1	0.6	—	3.3	3.3	3.7	—
8	2.50	2.49	2.25	—	0.901	0.787	0.859	—	5.6	1.0	0.5	—	5.9	7.6	6.1	—
9	2.50	2.47	2.31	—	0.878	0.715	0.694	—	7.7	3.2	1.2	—	3.3	3.5	3.8	—
10	2.46	2.39	2.38	—	0.878	0.663	0.650	—	7.2	1.7	0.8	—	3.2	3.1	3.7	—
11	—	—	—	2.17	—	—	—	0.60	—	—	—	—	—	—	—	1.45
12	—	—	—	2.20	—	—	—	0.620	—	—	—	—	—	—	—	1.52
13	2.42	2.54	2.36	—	0.738	0.459	0.507	—	—	—	—	—	—	—	—	—

* Each value represents averages of three replicates.

† See table 3.

‡ Phosphorus remaining after subtraction of seed and treatment phosphorus (11 mgm. P in 100 seedlings grown in sand alone).

§ P = Pima clay loam (virgin); Mv = McClellan clay loam (virgin); Mc = McClellan clay loam (cultivated); s = silica sand.

oat straw added with algal material or H_3PO_4 made no marked difference in yield. A highly significant difference in seedling yield, however, was found between different soils. The fertile Pima soil yielded a greater weight of barley than the cultivated McClellan soil. This agrees with expectations based on the analyses of the soils shown in table 3. The virgin McClellan soil was intermediate with respect to dry weight of seedlings.

Total phosphorus. Barley seedlings grown on the Pima soil were consistently higher in phosphorus than those on the two poorer McClellan soils (table 4). The differences for all treatments are highly significant. Seedlings grown in silica sand contained a higher percentage phosphate than did those grown in soil, but because of the lower dry weight of material, the total phosphorus uptake was less.

Data in table 4 also show that as the phosphate applications in the form of

algal material or liquid H_3PO_4 were increased from 150 to 600 pounds P_2O_5 per acre the total phosphate content of the seedlings increased. This characteristic is more pronounced in the McClellan than in the Pima soil. Pima clay loam is abundantly supplied with available native phosphate, whereas the McClellan soils are deficient, according to evaluations based on the CO_2 -extraction method.

Phosphate content of the seedlings was not changed significantly as a result of additions of oat straw. Narrowing the C/N of the straw from 22 to 15 in the algae plus straw treatment or from 249 to 22 in the H_3PO_4 plus straw treatment by additions of nitrogen did not influence the amount of phosphorus absorbed by the plant. The short period of growth, the high rate of P application, and the low total uptake of phosphorus by the seedlings probably did not allow the influence of the straw to be registered. Inasmuch as the C-P ratios of the treatments were small and varied only between 12 and 26, no influence on the phosphorus status of the seedlings was found. An experiment designed to demonstrate such an influence is reported later.

Uptake of labeled phosphorus from treatments. According to table 4, the uptake of phosphorus from algal material and H_3PO_4 by seedlings was as great in the cultivated McClellan as the Pima clay loam. An analysis of the data shows that the influence of a greater yield of seedlings and a lower proportionate demand for applied phosphate from the more fertile virgin soils is counterbalanced in the cultivated McClellan by a lower yield but a proportionately greater demand for applied than native phosphorus. Figure 1 brings this point out.

The amount of CO_2 -soluble phosphorus in the soils is directly correlated with the utilization of phosphorus from the algae and liquid H_3PO_4 .

Figure 1 also shows that, regardless of the soil, the percentage of phosphorus in the plant increased as the rate of application was increased. Both algal material and liquid H_3PO_4 share this characteristic. The phosphate from algae appears to be as available to seedlings as that of the wholly soluble liquid H_3PO_4 .

In presence of extracted oat straw of a high C/N and C/P, phosphorus of algal material and liquid H_3PO_4 was taken up in about equal amounts. Moreover, the presence of this highly carbonaceous material did not appear to influence the over-all uptake or the percentage phosphorus in the seedlings from the labeled treatments. Narrowing the C/N by addition of nitrogen to the straw had little effect on the percentage uptake of phosphorus from the algae or H_3PO_4 . These latter data were not plotted in the figure because the values are nearly identical with those of the straw without nitrogen treatment.

Rate of availability of algal phosphorus

There is some indication (14) that organic phosphorus compounds are available to plants, though it is generally accepted that phosphorus absorption is by way of ionized inorganic phosphates. The rate at which phosphorus of biological materials such as that of algal material becomes available to plants depends on: (a) proportion of inorganic to organic phosphorus in the material; (b) fixation by chemical means in the soil; (c) fixation by microorganisms in the soil; and (d) rate of mineralization or release of inorganic phosphorus from organically bound

phosphorus. The last is brought about largely by the soil microorganisms. Earlier studies (2, 7) have showed that fixation of inorganic phosphorus is controlled almost wholly by the amount of available carbon present for microbial food. It follows that the food supply also controls the rate of release or mineralization of phosphorus that is organically combined.

The obvious lack of knowledge regarding the influence of the aforementioned factors on the rate of release, in a form available for plant use, of phosphorus in organic combination prompted considerable experimentation on calcareous Arizona soils.³

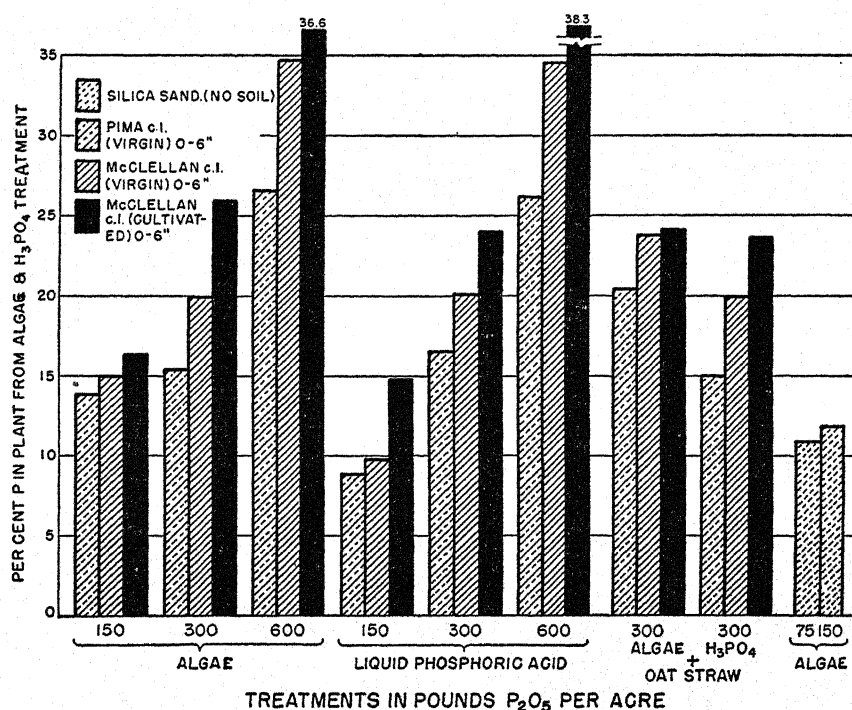


FIG. 1. Percentage Phosphorus in Barley Seedlings from Algal Material and Liquid H₃PO₄ Applied to Three Soils

Liquid H₃PO₄. Figure 2 affords a comparison between the rates of utilization of phosphorus as measured by percentage phosphorus in the plant derived from liquid H₃PO₄ applied to two soils. Since the root zone extends to all parts of the Neubauer pots, the amount of phosphorus absorbed by a growing plant from liquid H₃PO₄ applied to its root zone should depend only upon the rate at which the plant is capable of absorbing phosphorus in competition with the available native soil phosphorus. The slope of the curve in figure 2 from 1 day to the maxi-

³ Rogers, R. N. The rate of utilization of the phosphorus of algal cells by barley plants. 1951. [Unpublished master's thesis, Univ. Arizona.]

mum should, therefore, represent the maximum rate at which phosphorus can be utilized from any phosphorus application to the soil in question.

The McClellan soil, being poorer in available phosphorus than the Pima soil, produced seedlings having a higher percentage of their phosphorus from the H_3PO_4 treatment. The rate of uptake was similar in both soils. This appears to indicate that the same forces of fixation exist in the two soils in about the same relative proportion. The relationship between the amount of the phosphorus absorbed from H_3PO_4 applied to the McClellan soil as compared with that absorbed from H_3PO_4 applied to the Pima soil throughout the incubation is the same as that reported in figure 1.

The negative slope of the part of the curve extending from about 8 days to 21 days indicates that phosphate-immobilizing reactions in the soil had been allowed sufficient time to limit the availability of the phosphorus. These observations

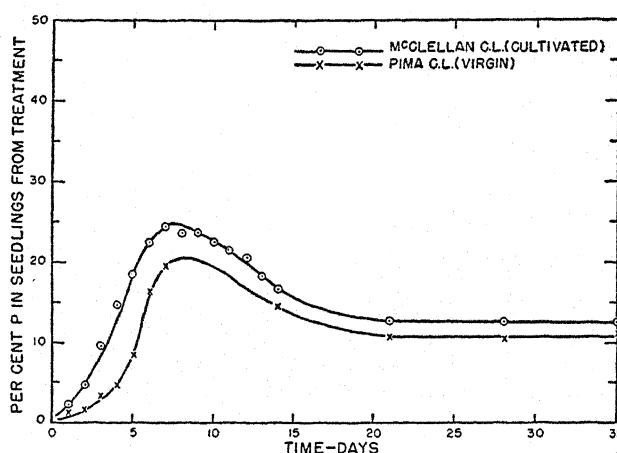


FIG. 2. Rate of Utilization of Liquid H_3PO_4 by Barley Seedlings Over a Period of 35 Days as Measured by Percentage Phosphorus in Plants from Treatment Applied in Two Soils

agree favorably with the rates of fixation of phosphorus reported by Hilbert *et al.* (8). After 21 days, phosphorus immobilization factors in the soils were in approximate equilibrium with those of mobilization.

Algal material. The slopes of the curves in figure 3 show the relationship between the rate of utilization of phosphorus of algal material added to McClellan and Pima clay loams. Since mineralization is defined as the conversion of organic phosphorus unavailable to plants into available inorganic phosphates, the curves in figure 3 do not represent rate of mineralization, but rather a balance between mineralization, on the one hand, and immobilization, on the other.

The rate of absorption of phosphorus from algal material was greater in the sand cultures throughout the entire 35-day period than in the two soils. Undoubtedly this was due, in part at least, to the absence of available native phosphorus in the sand. The difference in slope of the curves between the sand and soil cultures the first 21 days must be explained by other factors, however. Apparently

during this period the balance between the mineralization and fixation agents is slightly in favor of fixation in the soils compared with the sand, where fixation by chemical means is wholly absent and is limited only by biological factors.

Comparison of figures 2 and 3 shows that the rate of utilization of phosphorus from algal material was much lower than that of liquid H_3PO_4 during the first 8 or 9 days but it continued to increase to the sixteenth day. About the fifteenth day the two rates were equal. This explains the similarity between the utilization of algal and liquid H_3PO_4 phosphorus in the first experiment at the end of the fifteenth day of the culturing period. After about the sixteenth day the utilization of phosphorus from the algae exceeded that from the H_3PO_4 . Though there is a slight negative slope to all curves after the sixteenth day, equilibrium apparently is established between immobilization and mineralization.

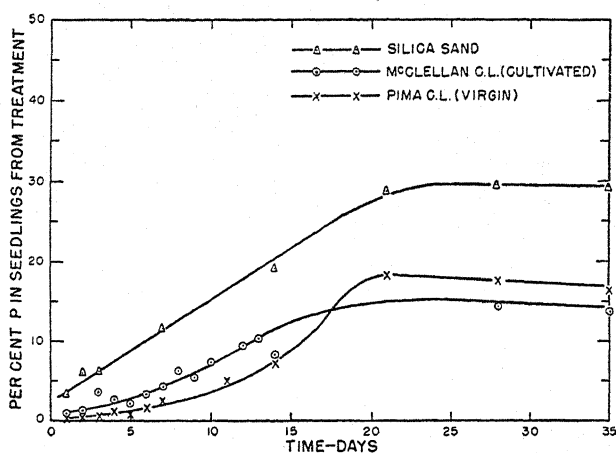


FIG. 3. Rate of Utilization of Phosphorus from Algal Material Over a Period of 35 Days as Measured by Percentage Phosphorus in Barley Seedlings from Algae Applied to Two Soils.

That there are marked characteristic differences between the *rate of utilization* of the phosphorus from algal material and liquid H_3PO_4 is due to fundamental differences between the two sources. Algal material is carbonaceous; not all the phosphorus is water-soluble and some of the organic phosphorus is not extractable with cold dilute mineral acids. The phosphorus of liquid H_3PO_4 , on the other hand, is wholly water-soluble. Although the water-soluble inorganic phosphorus of the H_3PO_4 as well as that of the algae presumably can be used instantaneously by the plant, the organically bound phosphorus of the algal material must depend upon enzyme activity of the plant roots (15) and soil microorganisms for conversion into available form.

Microbiological factor. To determine the influence of microbial activity on the availability of phosphorus from algal material and liquid H_3PO_4 , McClellan clay loam was sterilized in an autoclave, treated with sterilized algae and H_3PO_4 , and seeded to barley. The uptake of the phosphorus from the two sources was also

studied in sterilized and unsterilized sand cultures as a means of eliminating the influence of chemical fixation and isolating the effect of biological activity on phosphorus availability. The data obtained in this experiment are plotted in figure 4. The plants in the sterilized cultures were allowed to grow only 14 days, the maximum time during which the cultures could be kept free from microbial contamination.

Phosphorus absorbed from the sterilized treatments was significantly greater than that from the unsterilized cultures. The difference in utilization of the algal phosphorus appeared to be controlled largely by microbial activity. Although

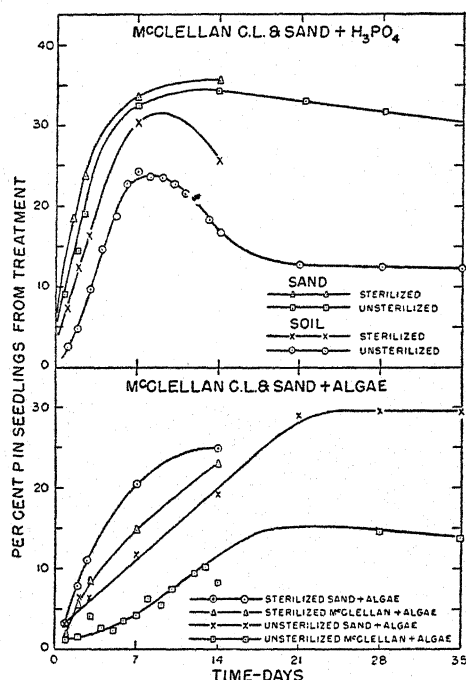


FIG. 4. Influence of Microbial Activity on Rate of Utilization of Phosphorus of Algal Material and Liquid H_3PO_4 Applied to McClellan Clay Loam

microbial activity appeared to limit the utilization of phosphorus of H_3PO_4 somewhat, chemical fixation appeared to be the dominant factor after the first week.

Total phosphorus uptake. Total uptake of phosphorus from algal material and liquid H_3PO_4 applied to Pima clay loam and to sand over a 35-day period is shown in figure 5. The results indicate that some chemical fixation, either precipitation or adsorption, by the soil took place rather rapidly the first few days after the phosphate sources were applied. Such fixation did not appear to influence the immediate uptake of the H_3PO_4 -phosphorus so much as that from algal material. The presence of organically bound phosphorus in the algal material, in addition to chemical fixation, probably was responsible for the poorer total uptake from

the algae during the first 2½ weeks. The greater uptake of phosphorus from the algal material than from H_3PO_4 after the third week furnishes evidence that: (a) algal material is more available to plants over longer periods; (b) chemical fixation is not so great a factor with the algal material as with liquid H_3PO_4 ; and (c) temporary conversion of available soil- or fertilizer-phosphorus into cell material by soil algae may be a desirable process from the standpoint of long-time availability. The hypothesis, supported by the data presented here, is that the soil algae remove available phosphorus from the sphere of chemical fixation by converting it into cell material or by absorbing luxury amounts that later may be released gradually for plant use.

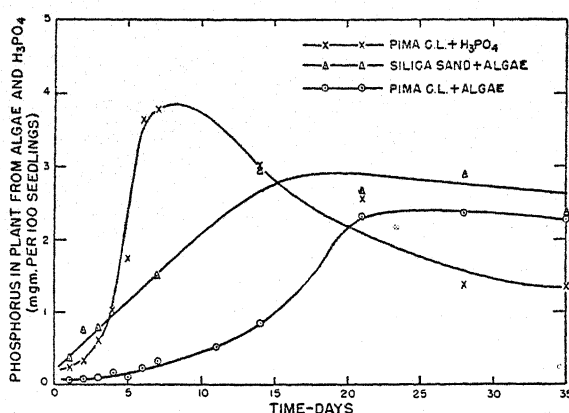


FIG. 5

FIG. 5. Rate of Uptake of Phosphorus of Algae and Liquid H_3PO_4 by Barley Seedlings in Pima Clay Loam and in Sand Over a Period of 35 Days as Measured by Total Phosphorus in Plant from Treatments.

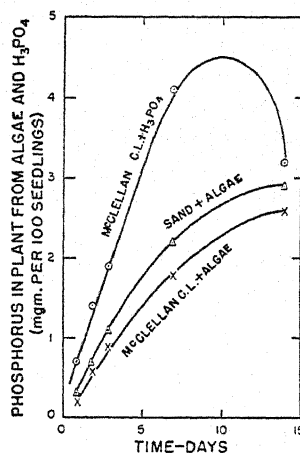


FIG. 6

FIG. 6. Rate of Uptake of Phosphorus of Sterilized Algae and Liquid H_3PO_4 by Barley Seedlings in Sterilized McClellan Clay Loam and Sand as Measured by Total Phosphorus in Plant from Treatment.

Total uptake data for *sterilized* cultures of McClellan clay loam and sand (fig. 6) indicate that there is a rather large proportion of phosphorus in the algal material that can be rapidly utilized by plants in absence of an active micropopulation. The total uptake of phosphorus from algal material compared with that from H_3PO_4 indicates that: (a) chemical fixation is less dominant with the organic source; (b) there is less *readily* available phosphorus in the algal material; (c) the activity of microorganisms exercises a greater influence on the utilization of phosphorus by plants from the algal material than do chemical factors.

Determination of the inorganic phosphorus in the algal material indicated that 82 per cent of the total phosphorus present was in this form. According to this value, phosphorus available for plant use apparently was abundant in the algal material, and uptake should be comparable to that of liquid H_3PO_4 . The marked lag in uptake from the algal material the first week, in comparison with liquid

H_2PO_4 , raises some doubt of the accuracy of the Pons and Guthrie method for determining inorganic phosphorus of algal material. Pons and Guthrie (14), as well as Kamen and co-workers (9, pp. 172-173), warn that some nonphytic organic phosphorus compounds may be appreciably hydrolyzed by the extraction solution used. An attempt was made to reduce hydrolysis to a minimum in the extraction of the algae by keeping the temperature of the extraction below 10° C. Nevertheless, the foregoing value for the inorganic phosphorus content of the algal material may be relatively high.

If it can be assumed that the total amount of phosphorus absorbed by the plants in the *sterilized* sand cultures represents the total amount of inorganic and easily hydrolyzable phosphorus present in the algal material, then the readily available phosphorus content of the algae can be estimated. Figure 6 shows that 2.9 mgm. of phosphorus was absorbed by the seedlings from the algae applied to the sterilized sand cultures; and since 4.4 mgm. of the phosphorus was applied, this would indicate a readily available phosphorus content of 65.9 per cent. This value compares favorably with the 55.4 per cent water-soluble and easily hydro-

TABLE 5

Effect of varying C-P ratios on percentage phosphorus in barley seedlings from algal material added to McClellan clay loam

TREATMENTS	PHOSPHORUS IN PLANT FROM ALGAE	C/P
	<i>per cent</i>	
Soil (unsterilized) + algal material.....	13.9	4.6
Soil (sterilized) + algal material + extracted oat straw.....	10.3	24.4
Soil (unsterilized) + algal material + extracted oat straw.....	7.8	24.4

lyzable organic and inorganic phosphorus reported for microbial tissues by Bartholomew and Goring (3).

Effect of C/P on availability of algal phosphorus

Phosphorus as well as nitrogen can be immobilized by microorganisms; therefore, addition of available carbon sources may be expected to increase microbial activity, resulting in a demand for phosphorus in proportion to microbial activity (7). To demonstrate the influence of crop residues on the availability of phosphorus to plants, extracted oat straw was added to sterilized and unsterilized McClellan soil with algal material, incubated 21 days, and seeded to barley, the Neubauer technique being used. A 21-day incubation period was used because a previous experiment involving no incubation prior to seeding was inconclusive. The barley seedlings were harvested in 15 days. Thus the phosphate source was in contact with the soil a total of 35 days.

The influence of organic plant material on the availability of phosphorus of the algal material is clearly shown in table 5. The presence of extracted oat straw had little effect on the availability of phosphorus in sterilized cultures. Utilization,

on the other hand, was significantly decreased by addition of oat straw to the unsterilized soil-algae cultures. Presence of the oat straw caused an increase in the activity of the micropopulation, which in turn increased the demand for available phosphorus, resulting in temporary immobilization.

SUMMARY

The comparative availability of the phosphorus of algal material and liquid H_3PO_4 to barley plants was studied by the Neubauer technique. Variations in rate of application, soils, time of incubation, micropopulation, and C-N and C-P ratios were considered.

Although the usual Neubauer method of testing soils for available phosphorus indicated that the phosphorus of algae and liquid H_3PO_4 is taken up in approximately equal quantities by barley seedlings in 15 days, a detailed study employing a modification of the Neubauer technique to determine the rate of uptake of the phosphorus over a 35-day period showed that there are characteristic differences in rate of utilization between the two sources.

The rate of utilization of phosphorus of liquid H_3PO_4 appears to be influenced to a greater extent by chemical than microbiological factors. This situation was reversed for the algal material. There also was some indication that over a long period the phosphorus of algae is slightly more available to plants growing in soils than is that of the wholly inorganic phosphorus of liquid H_3PO_4 .

The presence of available carbon and an active soil micropopulation appears to influence the rate of utilization of available phosphorus according to the C/P of the added material. Widening the ratio from 4.6 to 24.4 was shown to reduce, in the barley seedlings, the percentage phosphorus taken from the algal source.

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STANDARD FERTILIZATION AND THE QUALITY OF CROPS

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Received for publication February 19, 1952

It is generally supposed that acid soils are inferior to neutral or slightly alkaline soils in both quantitative and qualitative production of crops. Field trials have shown that proper liming will increase production and also improve the quality of the crops, for instance, by increasing Ca content. Consequently, liming is recommended for acid soils.

In the writer's experience, however, a deficiency of P in the feed of domestic animals is far more common than a deficiency of Ca. Analyses of Swedish soils (3, 4) have also disclosed that a deficiency of P is very common in acid soils. The content of readily soluble Ca is generally several hundred times larger than the content of readily soluble P. For improvement of the acid soils, and probably also for improvement of the crops grown on such soils, addition of P must be of greater importance than addition of Ca.

Standard fertilization (1, 3, 4) is based on the results of a reliable soil analysis, and therefore the deficient nutrients are added in sufficient quantities to bring about an appropriate nutritional standard in the soils, especially in acid soils. It has been shown that standard fertilization will increase the yields to such a degree as to make liming superfluous. This paper considers the influence of standard fertilization upon the quality of the crop.

MATERIALS AND METHODS

Standard fertilization was tried in field experiments on more than 50 farms in various parts of Sweden, the humidity of the climate being the main factor observed (3, 4). A few of the soils were neutral, though most of them were acid. The lowest pH value encountered in mineral soils was 5.2, but in humus soils values as low as pH 4.3 were found. On each experimental field, samples of topsoil (0-20 cm.), of subsoil (20-40 cm.), and of lower layers down to 100 cm. were collected and analyzed for readily soluble plant nutrients according to the writer's method (1, 3, 4). On the basis of the analytical data, the quantities of artificial fertilizers needed, in addition to the quantities of farmyard manure commonly used, to bring about standard fertilization were calculated. All soils were found to require P; phosphate fertilization therefore proved to be of the greatest importance. Addition of K was needed in about 75 per cent of the experimental fields. N was applied in small quantities only.¹

In every case the whole experimental field first received standard fertilization and then was divided into unlimed plots and plots limed to $\frac{1}{32}$, $\frac{1}{16}$, $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{1}{1}$ (full) lime-absorbing capacity of the topsoil, determined according to the

¹ According to the soil analyses, only P, K, and N were required. Sufficient quantities of Ca, Mg, Mn, and other plant nutrients were found to be present in the soils studied.

method of Jensen (6). Full liming denotes the amount of slaked lime per hectare required to bring the topsoil layer to pH 7.0. On mineral soils, this was generally 10 to 30 tons; on humus soils, up to 48 tons.²

The experimental fields followed the usual crop rotation of the farm. A typical one was: 1, fallow (start of experiment); 2, winter grain, mostly wheat; 3, spring grain; such as wheat, oats, or mixed grain; 4, hay; 5, hay; 6, hay or winter wheat; 7, oats or mixed grain. The hay crops were a mixture of clover, mostly red clover, and timothy grass. In some cases root crops or potatoes were included in the rotations. Samples of the crops were collected at harvest time, and the quality was determined in various ways.

TABLE 1

Influence of liming the soil on botanical composition of hay on standard-fertilized fields

SOIL TYPES AND PLANTS	DEGREES OF LIMING						
	0	1/32	1/16	1/8	1/4	1/2	1/1
Mineral soils							
Clover.....per cent	52.35	51.62	50.99	50.96	50.24	49.44	49.24
Grasses.....per cent	42.12	42.63	43.35	43.56	43.96	44.68	44.82
Weeds.....per cent	5.53	5.75	5.66	5.48	5.80	5.88	5.94
Humus soils							
Clover.....per cent	25.62	24.86	26.21	25.52	26.68	26.35	26.38
Grasses.....per cent	68.28	68.32	68.00	68.48	67.40	67.64	67.12
Weeds.....per cent	6.10	6.82	5.79	6.00	5.92	6.01	6.50

RESULTS

Botanical composition of hay

When the hay was cut, the composition of the stand was determined. The results are shown in table 1. Obviously, liming (and soil reaction) had very little influence on the botanical composition of hay when the nutritional standard was satisfactory. The type of soil, on the other hand, had a great influence.

Mineral constituents of hay

The clover and grasses in the hay were analyzed. The mean values of 67 harvests of clover are shown in table 2. The influence of liming was slight. There was a small increase of N from 1.89 per cent on unlimed plots to 1.96 per cent on fully limed plots. There was also a small increase in P. Probably the increases were more apparent than real. Table 1 shows that the percentage of clover tended to decrease on mineral soils with increased liming. This implies that clover becomes suppressed by the grasses and at harvest time is less well developed than that on unlimed plots. It is a well-known fact that the percentage of mineral constituents decreases with age. In other respects, liming had no influence. It is especially to

² Slaked lime was added solely for the purpose of changing the pH of the soil. The question was: Does standard fertilization increase fertility to such a degree that yields are unaffected by liming?

be noted that the Ca content was not affected by liming. In standard-fertilized soils the uptake of nutrients is apparently unaffected by liming and soil reaction. The analyses of grasses gave similar results, except that liming and soil reaction had no influence on the uptake of N and P. The Ca content alone increased slightly (3).

TABLE 2

Influence of liming the soil on contents of nitrogen and certain mineral constituents of clover hay on standard-fertilized fields

Results on total-weight basis

DEGREE OF LIMING	ANALYSIS OF CLOVER							
	Dry matter	N	P	Si	Ca	K	Mn	Mg
	%	%	%	%	%	%	%	%
0	85.00	1.89	0.164	0.068	1.07	1.06	0.0025	0.308
1/32	85.00	1.84	0.158	0.091	1.10	1.03	0.0020	0.336
1/16	85.00	1.91	0.168	0.077	1.07	1.07	0.0025	0.326
1/8	85.00	1.91	0.168	0.077	1.06	1.07	0.0028	0.304
1/4	85.00	1.93	0.169	0.063	1.07	1.03	0.0024	0.318
1/2	85.00	1.93	0.171	0.064	1.07	1.05	0.0023	0.302
1/1	85.00	1.96	0.171	0.074	1.08	1.03	0.0021	0.299

TABLE 3

Influence of liming the soil on contents of nitrogen and certain mineral constituents of grain mostly wheat

Results on total-weight basis

DEGREE OF LIMING	ANALYSIS OF GRAIN							
	Dry matter	N	P	Si	Ca	K	Mn	Mg
	%	%	%	%	%	%	%	%
0	87.00	1.71	0.323	0.015	0.034	0.26	0.0019	0.094
1/32	87.00	1.70	0.337	0.013	0.032	0.27	0.0020	0.093
1/16	87.00	1.69	0.324	0.009	0.033	0.27	0.0020	0.096
1/8	87.00	1.69	0.330	0.010	0.033	0.28	0.0019	0.101
1/4	87.00	1.71	0.335	0.012	0.034	0.28	0.0019	0.098
1/2	87.00	1.73	0.334	0.009	0.033	0.28	0.0019	0.101
1/1	87.00	1.73	0.336	0.007	0.032	0.28	0.0019	0.103

Mineral constituents of grain

Table 3 shows the results of analyses of 53 harvests of winter wheat, spring wheat, and winter rye, grain mainly for human consumption. Obviously, liming exerted only a slight influence on the composition of the grain. The nitrogen content increased from 1.71 per cent to 1.73 per cent, and phosphorus from 0.323 per cent to 0.336 per cent or about 4 per cent. The content of calcium has not increased.

Analyses of 61 harvests of oats gave similar results (3).

Weight of grain

The weight of 1,000 kernels of winter wheat, spring wheat, and oats was determined. No influence of liming could be detected, but climate and soil type had a marked influence (3). The kernels were heavier on mineral soils than on humus soils. A somewhat arid climate (yearly precipitation about 500 mm.) produced heavier kernels than did a somewhat humid climate (yearly precipitation up to 1,000 mm.). The weight per 100 liters of grain varied in the same manner, but no influence of liming was observed (3).

Baking quality of winter wheat

The baking quality of winter wheat, the first crop after liming, was determined on the harvests of nine experimental fields. The results are summarized in table 4. Of the qualities determined, only protein content and the volume of bread were slightly influenced by liming. In this case the protein content was more markedly influenced than the N content shown in table 3. The fact that

TABLE 4
Influence of liming the soil on the baking quality of winter wheat

QUALITIES DETERMINED	DEGREES OF LIMING						
	0	1/32	1/16	1/8	1/4	1/2	1/1
Dutch weight.....	126.0	126.8	126.6	124.9	127.2	124.6	125.7
Germination..... per cent	1.48	2.18	2.02	2.52	1.83	2.40	2.23
Molin units.....	29.7	29.0	29.8	30.2	29.3	30.7	30.0
Protein..... per cent	11.36	11.36	11.43	11.56	11.78	12.04	12.26
Dough per 100 gm. flour....	155.9	155.9	154.7	154.7	155.2	155.2	155.6
"Drop"..... degrees	132	129	134	136	131	127	122
Volume of bread..... cc.	550	552	554	559	573	578	575

baking quality was tested only on the first crop after liming explains the apparent influence in this case.

Feeding value of grain and hay as determined by chemical analysis

The feeding value of grain and hay was determined by official Swedish methods.³

Table 5 shows the mean values of analyses of eleven harvests of winter wheat, four harvests of spring wheat, and three harvests of winter rye. From the figures it is clear that there is a slight increase of pure protein, of digestible protein, and of crude fat due to liming. In other respects no influence of liming can be detected. Analyses of 15 harvests of oats gave very similar results (3).

The hay was generally cut at the flowering stage. Samples were collected during harvest and dried under cover. The samples were divided into clover, grasses, and weeds, of which the clover and grasses were analyzed. Table 6 gives the results of analyses of 24 harvests of clover. Obviously, liming did not influence

³ Statens Lantbrukskemiska Kontrollanstalt 1940 (Unpublished).

the composition to any appreciable degree. Analyses of 26 harvests of grasses gave even more closely similar results (3).

Weight of experimental animals fed crops

An analysis of a crop gives a number of data, but there may be other qualities in the crop than those determined by one or more analyses. If any such quality is of importance, from the nutritive point of view, this fact should be brought out by feeding experiments. For instance, palatability has a marked influence

TABLE 5
Influence of liming the soil on the feeding value of cereals

DEGREE OF LIMING	DRY MATTER	CRUDE PROTEIN	PURE PROTEIN	DIGEST- ABLE PROTEIN	CRUDE FAT	CRUDE FIBER	SOLUBLE CARBO- HYDRATES	ASH
	%	%	%	%	%	%	%	%
0	87.00	12.33	9.32	8.68	1.49	1.91	69.59	1.68
1/32	87.00	12.07	9.28	8.90	1.50	1.85	69.91	1.67
1/16	87.00	12.13	9.52	9.12	1.55	1.90	69.79	1.63
1/8	87.00	12.35	9.57	9.12	1.55	1.86	69.59	1.65
1/4	87.00	12.08	9.59	9.19	1.63	1.84	69.81	1.64
1/2	87.00	12.11	9.66	9.20	1.63	1.88	69.74	1.64
1/1	87.00	12.52	9.71	9.22	1.60	1.79	69.44	1.65

TABLE 6
Influence of liming the soil on the feeding value of hay of clover

DEGREE OF LIMING	DRY MATTER	CRUDE PROTEIN	PURE PROTEIN	DIGEST- ABLE PROTEIN	CRUDE FAT	CRUDE FIBER	SOLUBLE CARBO- HYDRATES	ASH
	%	%	%	%	%	%	%	%
0	85.00	13.10	11.13	8.09	2.15	24.89	38.73	6.13
1/32	85.00	13.09	11.12	8.10	2.16	24.91	38.73	6.11
1/16	85.00	13.13	11.20	8.16	2.17	24.44	39.30	5.97
1/8	85.00	13.19	11.21	8.17	2.14	25.10	38.49	6.08
1/4	85.00	13.11	11.15	7.96	2.17	24.97	38.66	6.09
1/2	85.00	13.12	11.13	8.14	2.14	25.21	38.37	6.16
1/1	85.00	13.09	11.29	8.33	2.19	24.87	38.78	6.07

on the uptake of feed, and if the experimental animals are fed *ad libitum* the more palatable feed ought to produce a more rapid increase in weight. Eighteen experiments were carried out on rats fed mainly on grain, 12 on guinea pigs fed hay and grain, and 15 on rabbits fed hay and grain. A few typical experiments are summarized here.

Experiment 7 (rats). Winter wheat from experimental field K70 constituted the main feed in this experiment. Supplementary feeds comprised cheese, 0.25 gm. a day until the rats attained a weight of 70 gm.; gelatin, 0.5 gm. a day throughout the experiment; cod liver oil, one drop a day; tap water.

The experimental field K70 was laid out on medium clay, with a humus content

of 5.08 per cent and a pH of 5.6. The lime-absorbing capacity of the topsoil was 16 tons of slaked lime per hectare. Standard fertilization, the total for 7 years, was calculated as 40 tons farmyard manure, 13 kgm. N, 82 kgm. P, and 33 kgm. K per hectare.

The wheat was crushed and given *ad libitum*. The feeding value of the wheat, determined by analytical methods, showed a negligible increase in pure protein and digestible protein due to liming.

Three male and three female rats were included in each group. The experimental animals from a number of litters were distributed evenly among the groups. If a litter contained 14, which was not uncommon, it was possible to use two individuals for each of seven groups. Usually, however, only seven individuals from each litter could be used. The weight of the animals was recorded once

TABLE 7
Influence of liming the feed-producing soil on increase in weight of rats
Averages for six replicates

	DEGREE OF LIMING OF SOIL						
	0	1/32	1/16	1/8	1/4	1/2	1/1
Weight at start.....gm.	52.3	54.2	50.5	51.7	49.0	50.3	49.1
Gain							
1st week.....gm.	8.3	11.2	11.2	14.5	13.0	13.3	13.5
2nd week.....gm.	18.3	18.0	18.3	17.8	18.8	17.0	16.7
3rd week.....gm.	16.7	17.7	17.7	18.3	17.7	18.5	17.7
4th week.....gm.	15.2	13.8	13.0	13.8	14.3	11.7	13.8
5th week.....gm.	18.3	15.8	14.8	17.8	16.0	17.0	13.7
6th week.....gm.	8.3	12.0	8.7	11.5	11.0	9.3	11.5
7th week.....gm.	10.7	10.2	10.7	12.2	10.5	10.7	12.8
8th week.....gm.	8.0	10.8	8.2	12.7	10.2	11.7	10.5
Mean per week.....gm.	13.0	13.7	12.8	14.8	13.9	13.6	13.7

$$m = 1.1; m_{\text{diff.}} = 1.6.$$

a week. The results are shown in table 7. Clearly, there is no significant influence on the increase in weight of the experimental animals from the liming of the soil that produced the main feed. Moreover, the supplementary feeds were given in such small quantities that they could not possibly obscure any appreciable difference caused by liming.

Experiment 14 (rats). To bring out any possible difference in the feed caused by liming, the supplementary feeds were gradually reduced until only the main feed, grain, was given, although Hart and McCollum (5) have shown that rats are unable to survive for very long on a diet of grain only. In this experiment the rats were given only crushed wheat and distilled water for 11 weeks. The winter wheat was harvested on experimental field K51 (4). According to analyses, liming had virtually no influence on the composition of the grain except for a slight rise in P. Of 42 rats included in the experiment only one died during the experimental period. Weekly increase in weight per animal was very low: liming degree 0, 3.2

gm.; $\frac{1}{32}$, 2.9 gm.; $\frac{1}{16}$, 3.0 gm.; $\frac{1}{8}$, 2.9 gm.; $\frac{1}{4}$, 3.6 gm.; $\frac{1}{2}$, 3.1 gm.; and $\frac{1}{1}$, 3.5 gm. No significant difference in the gain in weight could be determined (3).

Experiment 3 (guinea pigs). The main feed, hay from experimental field K71, containing an average of 63 per cent clover, was given *ad libitum*. Supplementary feeds comprised (a) bread made of 1 kgm. "Gluten S," manufactured from wheat grain, plus 2 kgm. potato flour, plus 50 gm. $(\text{NH}_4)_2\text{CO}_3$. The daily ration was 3 gm. during the first 3 weeks and 5 gm. thereafter (b) swedes, 2 gm. per day during the first 3 weeks and 5 gm. thereafter. Tap water was given to the guinea pigs.

The experimental field was laid out on light clay with a humus content of 5.30 per cent and a pH, of 5.6. The lime-absorbing capacity of the topsoil was 19.2 tons of slaked lime per hectare. Standard fertilization, the total for 7 years, was calculated as 60 tons farmyard manure, 16 kgm. N, 78 kgm. P, and 50 kgm. K per hectare.

TABLE 8

Influence of liming the feed-producing soil on increase in weight of guinea pigs
Averages for eight replicates

	DEGREE OF LIMING OF THE SOIL						
	0	1/32	1/16	1/8	1/4	1/2	1/1
Weight at start.....gm.	205.8	211.6	191.0	193.5	201.0	207.1	194.0
Gain							
1st week.....gm.	25.4	28.3	23.4	20.8	26.9	24.1	24.7
2nd week.....gm.	20.3	13.3	19.6	22.8	19.4	17.9	19.8
3rd week.....gm.	16.0	22.5	15.9	10.8	14.1	11.6	10.8
4th week.....gm.	17.9	14.4	16.1	19.6	20.6	15.9	13.9
5th week.....gm.	17.0	18.9	20.7	19.5	19.5	20.3	17.2
6th week.....gm.	10.9	16.6	15.0	12.4	11.5	16.0	13.5
7th week.....gm.	19.0	22.1	18.9	19.5	21.5	13.7	20.1
8th week.....gm.	14.3	13.6	15.4	13.4	15.8	15.9	12.2
9th week.....gm.	16.5	20.4	19.6	17.8	19.0	19.6	15.5
Mean per week.....gm.	17.4	18.9	18.4	17.3	18.7	17.3	16.4

$m = 0.7$; $m_{\text{diff.}} = 1.0$.

The feeding value of the hay, clover, and grasses was determined individually by the customary analyses. No significant difference caused by liming could be detected. The experimental bread contained 13.09 per cent digestible protein, 53.44 per cent soluble carbohydrates, 0.014 per cent P, and 0.080 per cent Ca. It was intended to be a feed rich in "pure" nutrients and poor in salts and vitamins. The swedes furnished the necessary amounts of vitamin C.

Four male and four female animals comprised each group. The weight was determined at weekly intervals. In table 8 the average increases in weight are recorded. The results show that there is no significant difference between the groups. Liming on the field producing the main feed had no effect on the feeding value. The supplementary feeds were given in such small quantities that they could not have obscured any appreciable differences in the hay from limed and unlimed plots.

Experiment 11 (guinea pigs). The main feed was crushed oats from experimental field K66, given *ad libitum*. The supplementary feeds were hay from experimental field K60, 10 gm. per day, and vitamin C in drinking water (distilled water), 8 mgm. and ascorbic acid per 25 ml. water.

Full liming on experimental field K66 (pH 5.4) required 18.0 tons of slaked lime per hectare and on experimental field K60 (pH 5.8) 11.4 tons. Standard fertilization required only medium quantities of fertilizers. Analyses of the oats and of clover and grasses in the hay disclosed no significant differences caused by liming (3).

The feeding experiment was carried on for 11 weeks. The average weekly gains in weight per animal were as follows: no liming, 13.9 gm.; $\frac{1}{32}$, 13.8 gm.; $\frac{1}{16}$, 14.0 gm.; $\frac{1}{8}$, 13.8 gm.; $\frac{1}{4}$, 13.2 gm.; $\frac{1}{2}$, 13.6 gm.; and $\frac{1}{1}$, 14.2 gm.; m , 0.9; $m_{diff.}$, 1.2. No significant difference in feeding value caused by liming the land could be detected.

TABLE 9

Influence of liming the feed-producing soil on increase in weight of rabbits
Averages for four replicates

	DEGREE OF LIMING OF THE SOIL						
	0	1/32	1/16	1/8	1/4	1/2	1/1
Weight at start.....gm.	986	957	880	939	1005	902	908
Gain							
1st week.....gm.	201	152	187	152	173	172	166
2nd week.....gm.	260	239	212	237	208	201	235
3rd week.....gm.	199	153	192	203	184	186	193
4th week.....gm.	226	288	242	181	222	212	232
5th week.....gm.	208	176	204	230	185	190	208
6th week.....gm.	121	146	158	138	136	112	109
Mean per week.....gm.	203	192	199	190	185	181	191

$$m = 8.1; m_{diff.} = 11.5.$$

Experiment 6 (rabbits). The main feed, hay from experimental field K50, containing about 75 per cent clover, was given *ad libitum*. Supplementary feeds were experimental bread, 20 gm. per day and swedes, 25 gm. per day. Tap water was given to the rabbits.

The experimental field was on medium clay with a humus content of 3.08 per cent and a pH of 5.8. Full liming required 11.7 tons of slaked lime per hectare. Standard fertilization for 4 years required 20 tons farmyard manure, 20 kgm. N, and 80 kgm. P. No addition of K was found to be necessary. Analyses of the hay showed no influence of liming on the composition (3).

Two male and two female animals made up each group. The weights of the animals were recorded once a week. The results, shown in table 9, indicate no influence of liming on the feeding value of the hay.

Experiment 15 (rabbits). The main feed was oats from experimental field K100, given *ad libitum*. Supplementary feed was hay from experimental field K96, 30 gm. per day. Distilled water was given to the rabbits.

Field experiment K100 was on heavy clay with a humus content of 4.75 per cent and a pH of 5.9. Full liming required 16.7 tons of slaked lime per hectare. Field experiment K96 was on light clay with a humus content of 7.68 per cent and a pH of 5.6. Full liming required 20.8 tons of slaked lime per hectare. Standard fertilization required only medium quantities of fertilizers. Analyses of the oats disclosed a slight increase in digestible protein, from 7.07 per cent on unlimed plots to 7.85 per cent on fully limed plots. In the clover and grasses of the hay, the tendency was somewhat in the opposite direction (3).

The feeding experiment lasted 11 weeks. The increase in weight was much slower than in experiment 6. The proteins of the oats were not so satisfactory as the proteins of the hay. The average weekly increases in weight per animal were as follows: liming degree 0, 85 gm.; $\frac{1}{32}$, 88 gm.; $\frac{1}{16}$, 85 gm.; $\frac{1}{8}$, 85 gm.; $\frac{1}{4}$, 84 gm.; $\frac{1}{2}$, 78 gm.; and $\frac{1}{1}$, 88 gm.; m , 6.8; $m_{diff.}$, 9.6. No influence on the feeding value of the feeds could be detected from liming the land (3).

Bone development of experimental animals

It is generally believed that liming acid soils will improve the influence of crops on bone formation. Several methods were used, therefore, to determine the ossification of the bones of animals in the feeding experiments.

When the experimental animals were killed at the end of the feeding experiment, the thoracic cavity was cut open to observe any symptom of rachitis on the ribs. In rats and guinea pigs the characteristic swelling of the cartilage was observed in a few cases, but no connection between the swelling and the kind of feeds could be found. They were purely individual variations among the animals (3).

Histological studies also were made on sections cut from femurs. No influence exerted by the feeds upon the structure could be noted.

When the experimental animals were killed, the femurs were cut out, cleaned of all soft tissues, dried at room temperature, and analyzed for N, Ca, and P. The results, recorded in table 10, show several instances in which the feed undoubtedly influenced the chemical composition of the bones. Though lack of space prevents lengthy discussion, it can be said that liming of the feed-producing soil proved to have no beneficial influence on the ossification of the bones.

X-ray determinations on the femur and the metatarsal bones were made by the method of Åslander and Törnqvist (2). X-ray photographs were taken at the start, in the middle, and at the end of the feeding experiment. The results showed that liming the feed-producing soil had no influence on the ossification of the bones of the experimental animals.

Other effects on experimental animals

When the experimental animals were killed at the end of the feeding experiments the weights of vital organs—heart, liver, spleen, kidneys, and testes—were determined. Considerable differences in these weights were found, mostly connected with differences in live weight. When the weights of the organs were

expressed in percentages of live weights, however, no significant influence of liming the feed-producing soils could be detected.

The weights of the carcasses of the rabbits were determined and compared with the live weights. When hay was the main feed, the weight of the carcass was slightly less than 50 per cent of the live weight; the hay gave a lean body. Oats

TABLE 10
Influence of liming the feed-producing soil on chemical composition of the bones of experimental animals

GROUPS OF ANIMALS	DEGREE OF LIMING OF THE SOIL							Mean value
	0	1/32	1/16	1/8	1/4	1/2	1/1	
Rats								
<i>Main feed: wheat</i>								
N.....%	5.93	5.97	5.61	5.39	5.47	5.47	5.48	5.64
Ca.....%	19.46	19.53	18.49	18.39	17.96	16.92	14.41	17.88
P.....%	9.08	9.20	8.77	8.83	9.16	8.21	7.92	8.74
<i>Main feed: oats</i>								
N.....%	5.64	5.50	5.92	5.11	5.41	5.47	6.15	5.64
Ca.....%	16.53	15.97	16.46	16.23	15.91	15.74	16.53	16.19
P.....%	7.53	7.39	7.44	7.25	7.82	7.81	7.84	7.58
Guinea pigs								
<i>Main feed: hay</i>								
N.....%	4.33	4.32	4.53	4.65	4.64	4.55	4.21	4.46
Ca.....%	17.97	17.89	18.10	18.76	18.14	18.28	17.43	18.07
P.....%	8.40	8.57	8.53	8.63	8.59	8.51	8.28	8.50
<i>Main feed: oats</i>								
N.....%	5.63	5.80	5.89	5.53	5.83	5.54	5.38	5.66
Ca.....%	18.28	18.57	18.26	18.14	18.41	18.31	18.71	18.38
P.....%	8.94	8.50	9.07	9.02	9.09	9.12	9.08	8.97
Rabbits								
<i>Main feed: hay</i>								
N.....%	3.13	3.20	3.15	3.17	3.30	3.32	3.55	3.26
Ca.....%	15.84	15.70	15.78	15.66	15.89	15.94	16.95	15.96
P.....%	8.44	8.23	8.35	8.43	8.47	8.26	8.29	8.35
<i>Main feed: oats</i>								
N.....%	4.62	4.52	4.03	4.22	4.52	4.14	4.12	4.31
Ca.....%	20.40	20.44	20.76	20.12	20.44	20.38	20.21	20.39
P.....%	9.08	9.37	9.00	9.92	9.04	9.30	9.20	9.40

as the main feed gave carcass weights somewhat above 50 per cent of the live weights; more fat was produced. No influence of liming the feed-producing soils could be detected (3).

DISCUSSION

The common assumption that acid soils always produce inferior crops is not confirmed by the present investigation. Moreover, this investigation seems to be

comprehensive enough and the methods of determining the qualities are sufficiently numerous and thorough to give reliable results. All the results indicate that liming has very little or no influence on the quality of crops grown on initially acid soils. An exception is, perhaps, the baking quality of wheat harvested as the first crop after liming, in which case a slight improvement may be noted with increased liming to neutrality of the soil. Probably this represents an effect of the action of lime upon the organic matter in the soil. Liming will induce a more or less rapid decomposition of the organic matter (7), resulting in increased nitrate production. Again, it has been shown that proper nitrate fertilization of wheat will increase the gluten content of the grain and thus also the baking quality of the wheat.

In other respects no appreciable influence of liming on the quality of the crops has been detected. In other investigations, for instance, by Smith and Hester (8), it has been shown that liming exerted a very marked and very favorable influence on the quality of the crops. The conflicting results of the two sets of investigations are, in the writer's opinion, explained by the fact that the writer used standard fertilization on all the experimental fields (3, 4). Standard fertilization is calculated on the basis of a reliable soil analysis and by judging other crop-producing qualities besides the nutritive standard of the soil. Nutrients found in too small quantities in the soil are added in sufficient amounts to bring the nutritive standard of the soil up to the optimum so far as our present knowledge permits. There seems to be a likelihood of coming close to the optimum, as very heavy yields have been obtained on previously low-yielding acid soils. Additional support to the claim that standard fertilization probably has produced somewhat optimal nutritive conditions in the acid soils is afforded by the fact that the quality of the crops on standard-fertilized soil appears to be equal on unlimed plots and on plots increasingly limed to neutrality.

SUMMARY

Yields from field experiments on standard-fertilized acid soils unlimed and limed from $\frac{1}{32}$ to full lime-absorbing capacity, that is to neutrality, were tested in various ways to determine the influence of liming the soil on the quality of the crops.

Liming had no appreciable influence on the percentage of clover and grasses in hay or on the mineral composition of the plants.

Some grain crops, especially winter wheat harvested as the first crop after liming, showed a slight increase in nitrogen content with increased liming, and consequently a slight increase in protein content and baking quality, but in other respects no appreciable influence of liming could be detected.

The feeding value of either hay or grain, determined according to official chemical methods, was in general unaffected by liming. In some cases a slight increase in protein occurred with increased liming.

Comprehensive feeding experiments on rats, guinea pigs, and rabbits failed to disclose any difference in the feeding quality of the crops due to liming. Increase in animal weight was equal with feed from unlimed plots and from plots

limed up to neutrality. There was no influence on the ossification of the bones of the experimental animals.

The results of the investigation indicate that standard fertilization brings about an optimal nutritional standard in the soil, so that previously low-yielding acid soils produce such heavy yields and crops of such good quality that liming cannot materially improve the quantity or the quality of the yields.

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DETERMINATION OF CATION-EXCHANGE CAPACITY OF SOILS BY USE OF "VERSENATE"

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Received for publication November 12, 1951

Determination of the cation-exchange capacity provides valuable data on the characteristics of clays and soils. Many methods that yield similar values have been developed. The best of them involve considerable time and equipment. Among the accepted methods are those involving leaching with concentrated salt solutions, leaching with dilute acids, and electrodialysis. These methods have been outlined by Piper (7). Other methods are the use of a soxhlet extractor as described by Perkins *et al.* (5) and the isotherm method of Lewis (3). The methods outlined by Schollenberger and Simon (8) and Peech (4) may be accepted as outstanding.

Recently Cheng and Bray (2) reviewed the work of Schwarzenbach *et al.* (9, 10, 11) dealing with the use of "versenate" (disodium-dihydrogen ethylenediamine tetra-acetic acid) as a chemical reagent in determining the calcium and magnesium content of soil and plant material. They have described the chemistry of the reaction. The use of versenate to determine the hardness of water has recently been developed and has been described by the Bersworth Chemical Company (1). It seems evident that versenate could be a useful tool in determining the cation-exchange capacity of soils.

The proposed versenate method has the following advantages. The only equipment needed is a balance, funnels, beakers, wash bottle, burette, and chemicals. As calcium and magnesium have greater energy of adsorption than the ammonium ion, it is somewhat easier to saturate the clay or soil with a single ion. Likewise, many soils when saturated with a divalent ion have a lesser tendency to puddle than when saturated with the ammonium ion and therefore are theoretically somewhat easier to wash free from excess electrolyte. When calcium or magnesium is used to saturate the exchange complex, a versenate titration may be substituted for the Kjeldahl determination when the ammonium ion is used. The method as outlined makes it easy to determine when the excess cation has been washed from the mineral.

Among the disadvantages to be expected of the proposed method are the highly colored solutions resulting from soils rich in organic matter. These colored solutions make the determination of the exact end point somewhat difficult. This difficulty may be partly overcome by diluting the sample, reducing the size of sample, increasing the amount of indicator, and titrating in a light such as is given off by a soft white or daylight fluorescent bulb. It has been found helpful to place the light under the beaker in which the titration is made. Another dis-

¹ Contribution No. 477. Thanks are due the Bersworth Chemical Company for supplying "versenate."

advantage is that versenate will quantitatively titrate powdered CaCO_3 or MgCO_3 , and therefore a soil containing free lime will show a high cation-exchange capacity unless the proper correction is made.

VERSENATE METHOD AND ITS APPLICATION

The versenate method is as follows: One gram of the clay or soil is saturated with magnesium (or calcium) by placing it in a beaker containing 50 ml. of a normal magnesium (or calcium) acetate solution, transferring to a funnel, and washing 10 times with 20-ml. portions of the solution. The funnel should be allowed to run dry between the additions. The excess electrolyte is removed from the sample by washing with water or 80% ethanol if the filtration is slow.

The leachate may be tested for freedom from magnesium by addition of buffer, indicator, and a few drops of versenate. If there is magnesium in the leachate, the indicator will be red; in absence of magnesium, the solution will be blue.

When the leachate is free from magnesium, the tip of the filter paper is broken and the mineral is washed into a beaker with water, an excess of versenate is added, and the excess versenate is titrated with a standard magnesium solution. The indicator used for the magnesium ion is Erio Chrome Black T.² A 1 per cent solution in hydroxylamine hydrochloride has been found to be satisfactory. The versenate should be buffered to a pH of approximately 10 for use with the magnesium ion and the Erio Chrome Black T indicator. A satisfactory concentration for the versenate solution contains 12.5 gm. of the disodium salt per liter, and a liter can be buffered by adding 2.2 gm. of NH_4Cl and 2.8 ml. of NH_4OH . The versenate should be standardized against a solution of known magnesium concentration. A convenient concentration of the standard solution contains 0.5 gm. of magnesium per liter.

If calcium is used to saturate the soil, the leachate can be tested for freedom from calcium by the addition of buffer, versenate, a few drops of Erio Chrome Black T, and a few drops of the standard magnesium solution. As the calcium combines with versenate before magnesium does, a typical magnesium reaction will be obtained in presence of calcium. If preferred, the calcium leachate can be directly tested by adjusting the pH to 12.0 with NaOH , adding murexide³ as an indicator and a few drops of the versenate. The murexide end point is not so easily determined as is that of the Erio Chrome Black T.

Several representative minerals and soils from Kansas were selected for test purposes. The soils were gathered from several of the agronomy experimental fields scattered over Kansas from regions materially differing in rainfall and in parent material of the soil. These soils have been described by Perkins and Schrenk (6). In addition, a horizon of soil from section 32 of Kansas was tested, samples varying in depth from the surface to 17 feet. This soil is described by Olson.⁴ At the greater depth it contains free CaCO_3 .

² National Analine #587 (Bersworth Chemical Co.).

³ Eastman organic chemicals.

⁴ R. V. Olson. Unpublished data.

RESULTS AND DISCUSSION

Results obtained by the proposed versenate method, by a variation of this method, by leaching the soil with ammonium acetate, and by leaching the soil with NH_4Cl are presented in table 1. In 18 of the 20 soils and minerals tested by the four methods, comparable values were obtained. For soil sample R 104, the

TABLE 1

Cation-exchange capacity of soils as determined by a proposed versenate method and a standard ammonium method

SAMPLE	CATION-EXCHANGE CAPACITY			
	Mg/Mg*	Mg/Ca†	$\text{NH}_4\ddagger$	$\text{NH}_4\§$
	ml.	ml.	ml.	ml.
Cherokee soil.....	19.2	19.6	18.9	17.2
Geary soil.....	13.6	14.3	13.9	12.9
Wabash soil.....	24.8	23.7	23.9	22.2
Columbus field 0-6 inches.....	8.3	8.3	8.6	8.9
Columbus field 6-20 inches.....	15.2	12.7	15.2	13.6
Wichita field 0-6 inches.....	15.8	15.9	17.2	14.3
Wichita field 6-20 inches.....	20.0	20.1	22.0	20.3
Meade field 0-6 inches.....	15.8	14.6	15.7	12.8
Meade field 6-20 inches.....	19.6	19.0	19.9	18.2
Dodge field 0-6 inches.....	16.2	17.1	18.0	17.5
Dodge field 6-20 inches.....	23.4	24.8	27.1	25.4
Manhattan field 0-6 inches.....	22.1	24.0	21.2	18.2
Wyoming bentonite.....	72.9	lost	74.8	66.5
California bentonite.....	103.5	102.0	106.3	106.0
Kaolin.....	4.2	6.6	5.3	6.1
Muscovite.....	3.9	2.1	2.1	3.0
R 97 0-18 inches.....	21.6	18.9	18.6	17.1
R 98 18-40 inches.....	20.2	30.5	30.4	28.6
R 101 120-150 inches.....	20.8	19.6	21.9	21.0
R 104 206-234 inches.....	61.2	53.7	11.3	6.1

* Samples saturated with magnesium, excess versenate added and back-titrated with magnesium.

† Samples saturated with calcium, excess versenate added and back-titrated with magnesium.

‡ Samples saturated with ammonium by leaching with neutral $N \text{ NH}_4\text{Cl}$, and ammonium determined by a Kjeldahl distillation with MgO .

§ Samples saturated with ammonium by leaching with neutral $N \text{ NH}_4\text{Ac}$, and ammonium determined by a Kjeldahl distillation with MgO .

versenate method gave appreciably higher results than the other methods. This difference is attributed to free CaCO_3 in the soil. No explanation has been found for differences in results obtained for soil R 98, and sufficient sample for further investigation was lacking. The recommended procedure for the versenate method is to saturate the complex with either magnesium or calcium acetate. Take the mineral up in an excess of versenate and back-titrate with magnesium acetate at pH 10.0. If the calcium-saturated minerals are back-titrated with the calcium

and the murexide indicator, the end point of the reaction is obscured by the color of the soil suspension and accurate end points are difficult to obtain.

Comparison of the results obtained by the four methods shows good agreement, and the differences are not sufficient in most cases to indicate outstanding differences between methods.

In general, leaching with ammonium acetate yields lower cation-exchange figures than does leaching with NH_4Cl . This might be explained by greater loss of organic matter due to its greater solubility in the acetate. The leachate from the ammonium acetate was considerably darker than that of the NH_4Cl . Other comparisons are possible, but it is felt that the versenate method will enable satisfactory determination of cation-exchange capacity. It is also suggested that versenate may be used to remove CaCO_3 and MgCO_3 from soils before cation-exchange capacity is determined, so that the figures obtained for the exchange capacity of the residue would be more accurate. It is also suggested that versenate may be useful in determining certain mineral species in the soil.

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CATION-EXCHANGE GROUPINGS IN THE SOIL ORGANIC FRACTION

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Received for publication March 31, 1952

The cation-exchange property of soil organic matter, although apparently recognized soon after Way's original discovery of base exchange in soils, has received much less intensive study than that of inorganic soil constituents. The comparatively very high exchange capacity of soil organic matter and preparations derived from it would seem to justify greater emphasis on the role of these materials in cation-exchange reactions of soil. Undoubtedly, the slow progress in this field is due partly to the extreme complexity of the systems involved. At present, information concerning the chemical nature of so-called humus is still very inadequate, in contrast to the rather definite picture of clay mineral structure. In the investigation reported here an attempt was made to characterize the groupings capable of cation exchange by functional group analysis without attempting to determine the structure of the complex molecules to which the groups are attached. Techniques that have proved useful in wood chemistry were employed.

According to McGeorge (7), lignin, lignocellulose, lignohemicellulose, or related substances are chiefly responsible for the exchange properties of soil organic matter. He found a linear relationship between the lignin content and cation-exchange capacity of organic matter, and attributed the exchange reaction to phenolic hydroxyl groups in the lignin molecule. Mitchell (8) suggested that lignin or a derivative is the constituent responsible for cation exchange in soil organic matter. Muller (9) concluded that cation-exchange properties in several fractions of decomposing organic materials obtained by various rather drastic chemical procedures could be explained only by the presence of such groups as carboxyl and hydroxyl in several different compounds. Gillam (6) was able to effect a small reduction in the exchange capacity of so-called humic acid preparations by acetylation and methylation of hydroxyl groups, and produced a somewhat larger reduction in the exchange capacity of lignin preparations by the same treatments. By means of potentiometric titrations he demonstrated the presence of carboxyl groups in the humic acids.

This investigation attempts quantitatively to relate cation exchange in the soil organic fraction with groupings capable of furnishing acidic hydrogen.

MATERIALS AND METHODS

Several preparations fairly high in organic matter and free of inorganic exchange minerals were obtained by treating soil samples with HCl and HF according to the method of Rather (10) as modified by Alexander and Byers (1) for the determination of soil organic matter. This treatment leaves the organic fraction largely intact while dissolving a large portion of the mineral matter,

due chiefly to decomposition of the hydrated aluminosilicates. Partial hydrolysis of organic matter probably occurs, but the amount of material brought into solution is usually less than 10 per cent of the total, and therefore the residue is reasonably representative of soil organic matter *in situ*. The masking effect of clay on some of the reactive groupings, whether of a physical or chemical nature, is of course removed by the combined acid treatment. Seven soil samples were treated in this manner, including a peat and a pine forest soil from California, and the A₁ horizon of Dunkirk, Ontario, two Honeoye, and Yates soil series in New York.

Methylation with diazomethane

Twenty-gram samples of the acid-treated preparations were suspended in 100 ml. dry ether containing approximately 5 gm. of diazomethane prepared from nitrosomethylurea by the method of Arndt (2). The flasks containing the samples were kept below 0°C., and the suspension was either stirred mechanically or allowed to stand until the diazomethane was consumed as indicated by the disappearance of the yellow color. The ether was then filtered off, and the samples were dried for analysis. Methoxyl content was determined by Clark's modification of the method of Vieböck and Schwappach (4) except that the reaction time was extended to 1½ hours, which was required for quantitative demethylation of the organic materials. Cation-exchange capacity was determined by leaching a sample of appropriate size (0.5 to 2.0 gm.) with 250 ml. of 0.1 N barium acetate, washing with water, then leaching with 0.1 N HCl. Barium was determined in the acid leachate by means of the Beckman flame spectrophotometer or gravimetrically as the sulfate, depending on the quantity present.

A separate sample of the methylated product was refluxed with N KOH in 50 per cent acetone to saponify the methyl ester. The acetone was then distilled off, the solution acidified, and the precipitate filtered off and dried.

The methylation procedure was repeated on each sample until no additional methyl groups could be introduced.

Methylation with dimethyl sulfate

Twenty-gram samples of the organic materials were allowed to react with 2 ml. dimethyl sulfate in the presence of 100 ml. 0.2 N KOH in an atmosphere of nitrogen. After each treatment, the suspension was acidified and the precipitate filtered off and washed, dried, and reground. Since this treatment involved a loss of organic matter, determinations of carbon, hydrogen, and organic matter were made, and methoxyl and cation-exchange capacity were determined as previously described. In certain samples, exchange capacity toward Ba(OH)₂ was determined by allowing a 0.5-gm. sample of the organic material to stand overnight in an excess of the alkali, after which the unused Ba(OH)₂ was titrated potentiometrically. To minimize the solvent effect of the alkali on the organic matter, some of the samples were also methylated in ether medium containing solid KOH.

The methylation procedure was repeated until no further reduction in ex-

change capacity occurred, after which the samples were treated with diazomethane until a fully esterified product was obtained.

Specificity of reagents

Diazomethane and dimethyl sulfate have been widely used by lignin chemists to determine carboxyl and phenolic and alcoholic hydroxyl groups, since diazomethane presumably will react with carboxyl and phenolic hydroxyl groups, whereas dimethyl sulfate will react with both types of hydroxyl but will not esterify carboxyl in an alkaline solution. Diazomethane is not specific for phenolic and carboxylic hydroxyl, however, and will react with acidic hydrogen in several other ways. According to Eistert (5), diazomethane will react with keto-enol compounds to form either an ether or a C-methyl derivative, depending on the relative strength of the keto or enol form, and will form N-methyl derivatives of compounds where the acidity of the hydrogen attached to nitrogen is enhanced by adjacent carbonyl. Alcoholic hydroxyl can also be methylated by diazomethane if acidifying groups are adjacent. Spencer and Wright (11) have questioned the usefulness of diazomethane in lignin chemistry in view of its reaction with lactones involving methylation and pyrazoline formation. Side reactions with diazomethane are minimized in ethereal solution because of the neutralizing effect of the solvent on weakly acidic compounds. For this reason, ether was employed in this work. Groupings capable of dissociating sufficiently to function in cation exchange will probably react with diazomethane.

Dimethyl sulfate will methylate all groupings capable of reacting with diazomethane except carboxyl as well as more weakly acidic groupings not affected by the latter reagent. The likelihood of side reactions is much greater in the strongly alkaline medium employed.

RESULTS

Data obtained from diazomethane treatment of the organic preparations are shown in figure 1. It is clear that groupings capable of exchanging cations are blocked by methylation with this reagent, since there is a high negative correlation between the total methoxyl content and exchange capacity in all cases. The increase in methoxyl was somewhat greater than the corresponding decrease in exchange capacity, as indicated by the values of the slope b , which all fall between -1 and -2 . This suggests the occurrence of a reaction or reactions of the type described by Spencer and Wright (11) in which the methoxyl content is increased through opening of a lactone ring rather than by methylation of hydroxyl. Quantitative interpretation of these results is further complicated by the failure of diazomethane to block completely the cation-exchange groupings in any case except the Ontario sample, although it was reduced to a very low value in the Yates and Honeoye A samples. This may have been due to steric hindrance, the depressing effect of the ether solution on ionization, or other unknown factors. An additional treatment of the peat with diazomethane in dioxane did not alter its exchange capacity.

The increase in methyl ester after each methylation, as estimated by loss of

methoxyl by saponification, was highly correlated with decrease in exchange capacity in the peat and pine forest soils but not significantly correlated in the Dunkirk soil because of too few points (fig. 2). In other words, the decrease in exchange capacity after each treatment was directly proportional, though

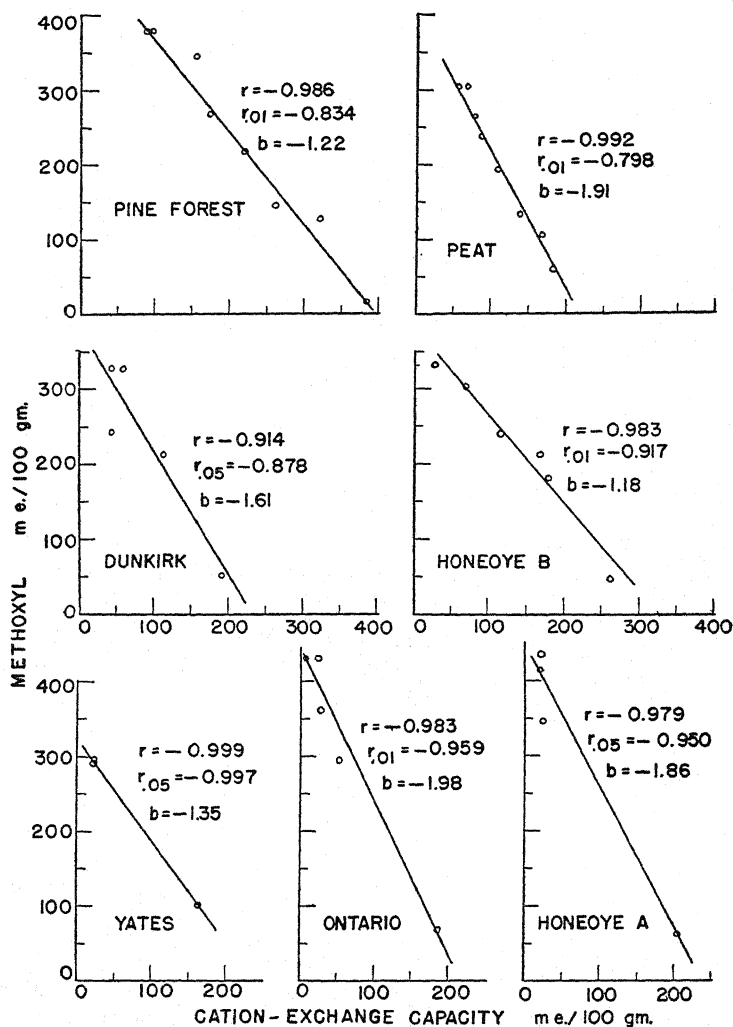


FIG. 1. Correlation Between Total Methoxyl Content and Cation-Exchange Capacity of Diazomethane-Treated Samples

not exactly equivalent, to the number of carboxyl groups blocked. The other four samples were saponified only once, after the final diazomethane treatment.

Reduction in exchange capacity was also effected by treatment with dimethyl sulfate, as shown in tables 1 and 2, although the reduction was in no case so great as with diazomethane. The fact that most of the decrease in exchange

capacity occurred during the first one or two methylations indicates that hydrogens sufficiently acidic to function in cation exchange were readily replaced with methyl, and that further increases in apparent methoxyl were due to reaction with groupings not involved in exchange. The treatments in ether medium had comparatively little effect on either methoxyl content or exchange capacity. The errors in the data of table 2 are rather large because of the low

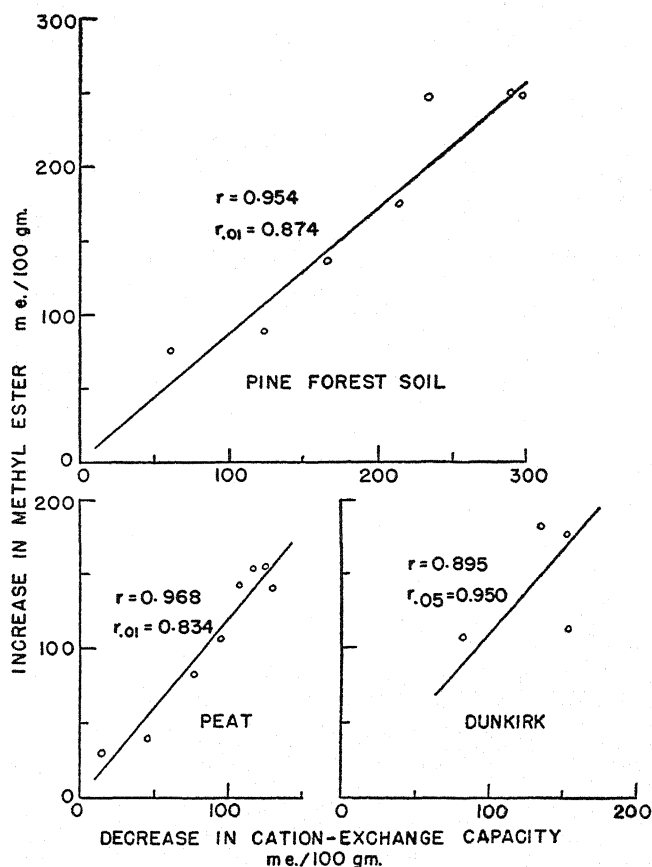


FIG. 2. Correlation Between Increase in Methyl Ester and Decrease in Cation-Exchange Capacity of Diazomethane-Treated Samples

organic content of the samples and the losses of organic matter during treatment. An error of 0.05 per cent in the methoxyl determination corresponds to 23 me. on the organic matter basis in Yates soil, for example, and an error of 1 me. in the cation-exchange capacity of the original sample would amount to 14 in the tabular data. Although corrections for losses of organic matter due to solubility were applied by determining the organic content at each step, there was no way to correct for qualitative changes in the organic matter remaining. The data for the two Honeoye samples are more reliable in view of their higher

initial organic content, and these are in general argrement with the data of table 1.

When phenolic hydroxyl and possibly other functional groups are blocked in this manner by treatment with dimethyl sulfate, the remaining exchange capacity presumably is due solely to carboxyl groups. This was confirmed by esterification of the dimethyl-sulfate-treated materials with diazomethane, which resulted in complete or nearly complete loss of exchange capacity, as shown in table 3.

TABLE 1
Methoxyl content and cation-exchange capacity of materials treated with dimethyl sulfate
Results in me./100 gm. organic matter

NUMBER TIMES METHYLATED	METHOXYL	EXCHANGE CAPACITY BY		INCREASE IN METHOXYL	DECREASE IN EXCHANGE CAPACITY BY	
		Ba(C ₂ H ₃ O ₂) ₂	Ba(OH) ₂		Ba(C ₂ H ₃ O ₂) ₂	Ba(OH) ₂
<i>Peat</i>						
0	60	183	379	—	—	—
1	246	—	306	186	—	73
2	292	—	—	232	—	—
3	326	—	—	266	—	—
4	387	74	286	327	109	93
5	406	68	—	346	115	—
6	435	69	—	375	114	—
<i>Pine forest</i>						
0	17	385	690	—	—	—
1	44	309	—	27	76	—
2	169	247	449	92	138	241
3	192	218	463	175	167	227
4	247	211	461	230	174	229
<i>Dunkirk</i>						
0	87	193	427	—	—	—
1	213	144	339	126	49	88
2	313	136	257	226	57	170
3	361	126	234	274	67	193
4	358	122	240	271	71	187

The final values in all except the pine forest soil are within the limit of experimental error. The increase in methoxyl is almost invariably larger than the corresponding decrease in exchange capacity; thus it is obvious that although carboxyl groups probably account for the remaining exchange capacity after the dimethyl sulfate treatments, subsequent application of diazomethane results not only in esterification of these carboxyl groups, but also reaction at nonexchange sites. The number of these sites not blocked by dimethyl sulfate apparently was greater when an ether medium was used, since the discrepancies between

increase in methoxyl and decrease in exchange capacity, as shown in table 3, were greater than when pretreatment was carried out in aqueous medium.

Two independent estimates of the carboxyl content of the organic materials were obtained: one by saponification of the diazomethane-treated samples, and the other by the increase in methoxyl upon application of diazomethane to materials pretreated with dimethyl sulfate. The latter procedure has been

TABLE 2

Methoxyl content and cation-exchange capacity of organic matter treated with dimethylsulfate in aqueous and in ethereal alkali

Results in me./100 gm. organic matter

NUMBER TIMES METHYLATED	AQUEOUS		ETHEREAL	
	Methoxyl	Exchange capacity by $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$	Methoxyl	Exchange capacity by $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$
<i>Yates</i>				
0	101	164	101	164
1	180	107	100	146
2	306	111	124	172
3	326	95		
<i>Ontario</i>				
0	70	187	70	187
1	206	106	56	172
2	282	142	79	166
3	338	135	77	173
<i>Honeoye A</i>				
0	63	202	63	202
1	226	111	52	190
2	300	151	57	185
3	303	84		
<i>Honeoye B</i>				
0	49	263	49	263
1	215	219	68	204
2	243	194	51	193
3	272	129		

extensively employed by wood chemists for estimation of carboxyl. These figures, together with apparent uronic carboxyl, are compared in table 4. The very poor agreement between the first two columns is not particularly surprising in view of the evidence for side reactions with diazomethane mentioned previously. Obviously only one of the procedures, and perhaps neither, gives a valid estimate of the carboxyl content. If the order of magnitude of these figures can be relied upon, however, it may also be concluded that carboxyl groups

TABLE 3
*Methoxyl content and cation-exchange capacity of materials treated with diazomethane
 following dimethyl sulfate*
 In me./100 gm. organic matter

PRETREATMENT IN AQUEOUS MEDIUM				PRETREATMENT IN ETHEREAL MEDIUM			
Methoxyl	Exchange capacity	Increase in methoxyl	Decrease in exchange capacity	Methoxyl	Exchange capacity	Increase in methoxyl	Decrease in exchange capacity
<i>Dunkirk</i>							
419	34	61	88	377	23	198	123
438	14	80	108	386	24	207	122
506	3	148	119				
<i>Yates</i>							
509	12	183	83	255	57	131	115
				355	26	231	146
				413	9	289	163
<i>Ontario</i>							
474	7	136	128	140	140	63	33
				378	6	301	167
<i>Honeoye A</i>							
427	9	124	75	311	51	254	134
				359	15	302	170
				431	5	374	180
<i>Honeoye B</i>							
446	11	174	118	117	148	66	45
				290	41	239	152
				338	12	287	181
<i>Peat</i>							
516	1	81	68				
<i>Pine forest</i>							
329	140	82	71				
413	66	166	145				
493	28	246	183				
496	14	249	197				

other than the uronic type are present in the soil organic fraction, since the uronic figures are invariably lower than the estimates of total carboxyl.

DISCUSSION

Of the several possible sources of exchangeable hydrogen in the soil organic fraction, carboxyl groups, phenolic hydroxyl groups, and hydrogen attached to

nitrogen in heterocyclic compounds seem the most likely to be of importance on the basis of what is known about soil organic matter and its precursor, undecomposed plant residues. Carboxyl groups occur in the polyuronides, in aliphatic acids, and probably in oxidized side chains attached to lignin molecules; phenolic hydroxyl groups occur in lignin, in certain amino acids, and in tannins; heterocyclic nitrogen with adjacent acidifying groups occurs in the nucleic acids. These represent only a few of the more obvious possibilities. All three types of groups mentioned can be methylated with diazomethane, and the high correlation between methoxyl content and exchange capacity following diazomethane treatment indicates that these groupings function in cation exchange, although others may be of some importance. The reduction of cation-exchange capacity by alkaline dimethyl sulfate clearly indicates that carboxyl groups alone do not furnish all the exchangeable hydrogen. In the seven soil samples treated, between 37 and 62 per cent of the exchange capacity was eliminated by blocking phenolic hydroxyl and other groups capable of reaction with the dimethyl sulfate reagent.

TABLE 4

Total carboxyl estimated by two methods compared with apparent uronic carboxyl in organic preparations

In me./100 gm.

SAMPLE	CARBOXYL BY SAPONIFICATION	CARBOXYL BY DIAZOMETHANE	APPARENT URON- IC CARBOXYL
Peat.....	131	81	36
Pine forest.....	249	249	26
Dunkirk.....	176	148	72
Yates.....	91	183	71
Ontario.....	201	136	68
Honeoye A.....	190	124	84
Honeoye B.....	128	174	70

Estimation of carboxyl by direct titration with standard alkali was attempted, but constant drift in pH over a period of several days made this very difficult to do with any degree of precision. The only instance in which good reproducibility was obtained was in the titration of the peat sample; the carboxyl value of 130 me. agrees well with that obtained by saponification, 131 me. Attempts to determine carboxyl by back titration in an isopropyl-alcohol-ethylene-glycol medium likewise proved unsuccessful. The uronic carboxyl values are of interest in connection with Bremner's (3) criticism of methods for determination of polyuronides in soils. Although, as he suggests, cleavage of nonuronic carboxyl may occur in the conventional procedure, which involves refluxing with 12 per cent HCl for several hours, it seems unlikely that this is quantitative. The highest value obtained for uronic carboxyl, 84 me. per 100 gm., corresponds to 14.8 per cent of the organic matter accounted for as uronic anhydride.

The stoichiometry of cation exchange in the organic fraction is by no means so clear-cut as in the clay mineral fraction; therefore the determination of cation-exchange capacity is somewhat arbitrary, depending on the nature of the re-

placing cation as well as on the pH of the replacing solution. For example, the exchange capacity of the peat sample was 379 as determined by barium hydroxide, 296 by potassium hydroxide, 254 by NaOH, 183 by barium acetate, and 69 by potassium acetate. These differences can be explained in part by formation of inner complex compounds as well as normal salts by replacing cations; steric considerations are undoubtedly also important. In view of the complexity of the systems involved, anomalies in the experimental data obtained are not at all surprising. An additional source of error was alteration in the chemical nature of the materials treated in alkaline medium even though oxygen was excluded wherever possible. Solubility losses were appreciable, and the carbon content of the insoluble residue increased beyond that produced by the introduction of methyl, indicating solution of constituents lower in carbon than the bulk of the residue.

On the basis of the methylation studies, it can be concluded that the cation-exchange property of soil organic matter is due to functional groups capable of forming esters, ethers, methylimides, or possibly one or two other types of methyl derivatives. For the seven soil samples on which data were obtained, 46 ± 12 per cent reduction in exchange capacity was produced by dimethyl sulfate. If the total nitrogen content of the organic matter is assumed to be 6 per cent, it is probably safe to estimate that not more than one tenth, or 0.6 per cent, occurs as imide nitrogen, corresponding to about 45 me. exchange capacity. Thus, of the 46 per cent of the exchange groupings blocked by dimethyl sulfate, a maximum of about 25 per cent could be accounted for as imide nitrogen, with more probable figures in the range below 10 per cent, leaving in excess of 36 per cent due to phenolic and enolic hydroxyl. Presumably the other 54 per cent is due to carboxyl. Since the standard deviation from the mean of this group of samples is large, this figure is not in serious disagreement with that calculated from estimates of carboxyl by saponification, 74 ± 19 per cent of the total exchange capacity. At any rate, more than half the average exchange capacity is due to carboxyl. A major portion of these functional groups probably occur in the polyuronide and lignin-derived fractions. Other acidic groups in the soil organic fraction, such as phosphoric acid esters, do not occur in sufficient quantity to account for more than a small fraction of the total exchange capacity.

In spite of the many experimental difficulties involved, the application of functional group techniques to soil organic matter should prove very useful, and may provide information which otherwise might have to await more detailed information on the chemical nature of organic soil constituents.

SUMMARY

Organic preparations of several soils were obtained by treating them with a hydrochloric-hydrofluoric acid mixture to remove inorganic exchange minerals. These preparations were treated with diazomethane and dimethyl sulfate alone and in combination to block functional groups capable of furnishing acid hydrogen. Cation-exchange capacity and methoxyl were determined after each treatment.

In the diazomethane-treated materials the cation-exchange capacity was found to be inversely related to methoxyl content. Coefficients of linear correlation were significant in all cases. Increase in methyl ester was a linear function of decrease in exchange capacity. In one sample the exchange capacity was reduced essentially to zero by diazomethane.

Reduction in exchange capacity was also effected by treatment with dimethyl sulfate in alkali, though to a lesser degree than in the diazomethane treatment. Application of the latter reagent following dimethyl sulfate blocked all groupings capable of cation exchange.

Uronic carboxyl content as determined by boiling with 12 per cent hydrochloric acid was somewhat lower than estimates of carboxyl obtained by saponification and methylation procedures.

The ability of cation-exchange groupings in the soil organic fraction to form esters and ethers with methylating agents indicates that the majority of these groupings are probably carboxyl and phenolic or enolic hydroxyl.

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PENETRATION AND LOSS OF HEAVY APPLICATIONS OF BORAX IN FLORIDA MINERAL SOILS

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Received for publication March 10, 1952

Because of its extreme toxicity at high concentrations, borax has been employed as an effective herbicide. When it is used in such locations as railroad rights-of-way or petroleum refinery and storage grounds, residual effects do not constitute a problem. But in arable lands which are to be put into crop production subsequent to treatment, the rate of disappearance of the toxic effects is of definite economic interest. Hurd-Karrer (2), who used borax as a herbicide at the rate of about 440 pounds per acre, reported that its toxic effects persisted after 36 months in the soil, but this was in greenhouse experiments from which there was no leaching. Williams (7), who used borax on a medium loam in shallow boxes at the rate of 90 pounds per acre, found that it gave a heavy kill of buried viable seeds of both clover and weeds, but that resowing with clover after 35 days resulted in uniform and vigorous germination, while germination of weeds was still low.

Litzenberger, Post, and Morris (4), who used both borax and sodium chlorate as herbicides, found that borax eliminated the fire hazards encountered with chlorate, had a more delayed action, and greatly reduced seedlings which continually reinfested chlorate-treated land. Established stands of yellow toadflax (*Linaria vulgaris* Hill) were eradicated by a borax application of 7 pounds per square rod, while the serious range pest Klamath weed or St. Johnswort (*Hypericum perforatum* L.) was completely controlled by borax at 8 pounds per square rod. Fall applications of borax were most effective on the more porous, lighter soils where the limited precipitation (a mean of about 1.3 inches per month for most areas in Montana) was sufficient to leach the chemical into the soil by the time the roots became active in spring.

Stoddard (6) recommended borax at 10 pounds per square rod for eradication of poison ivy (*Rhus toxicodendron* L.) but warned that the herbicide should not be used near trees and shrubs that were to be preserved. Weathering and the use of lime were suggested as means of eliminating the residual toxic effects. Under heavy rainfall, the rapid solubility of borax (3, 10) favors its removal; but Purvis and Hanna (5) found no evidence of chemical fixation by lime. They reported that although Norfolk fine sandy loam in an overlimed condition retained more applied boron after leaching than did the same soil in an unlimed state, this retained boron remained available to plants. Removal by leaching appears, therefore, to be the most practical way to eliminate the toxic effects of borax.

The downward movement of boron from borax in the small amounts required

for plant nutrition was studied in the field by Kubota, Berger, and Truog (3), who found that the most rapid movement occurred in the lightest soils; and by Wilson, Lovvorn, and Woodhouse (8), who reported that within 6 months the borax application was almost completely lost from the surface 8 inches of Norfolk sandy loam, while in Cecil clay very little moved below the 8-inch depth. In the foregoing studies borax residuals were from applications of 10 to 40 pounds per acre, while the amounts employed as herbicides (2, 4, 6, 7) range from 90 to 1,600 pounds per acre.

The purpose of the present study was to investigate the rate of penetration and loss of heavy applications of borax in two diverse Florida soils. It has been shown that the sodium and boron from borax move somewhat independently in the soil; sodium enters into an exchange reaction, whereas boron moves more rapidly in association with various cations (3).

EXPERIMENTAL

The retention of borax was calculated by determining the residual boron in the different horizons and converting this to borax equivalent. The boron was determined as boiling-water extractable by a procedure described elsewhere (9).

The soils used were Arredondo loamy fine sand and Lakeland fine sand. Arredondo, of phosphatic origin, is a well-drained upland soil. The depth to clay was extremely variable, but was mostly in the range from 12 to 20 inches. The Lakeland soil was excessively drained, as depth to clay exceeded 48 inches. In both areas the reaction was about pH 5.6 for the topsoil, with slight variations in the lower depths.

Borax was applied to the Arredondo soil at rates of 0, 100, 400, and 1,600 pounds per acre on June 7, 1945. It was broadcast in a broad band just inside the extreme branch spread of 17-year-old pecan trees. The soil area was approximately 0.01 acre for each tree; the borax was applied at 0, 1, 4, and 16 pounds per tree. The soil remained undisturbed for several months, but was disked at infrequent intervals during the remainder of the experiment. The effects of the borax applications upon the trees were reported elsewhere (1). Toxic effects upon the moderate growth of volunteer weeds from the 1,600-pound application were striking but temporary, while toxicity from the 400-pound rate was moderate and from the 100-pound rate negligible. Preliminary determinations of soil boron early in the experiment indicated that penetration into the lower horizons had been so rapid that it would be necessary to sample to a considerable depth to obtain satisfactory evaluation. The samples, which were taken approximately 4, 12, and 24 months after the borax was applied, were obtained, therefore, at 0-3 and 3-7 inches and at each successive 7-inch depth down to 42 inches. Sampling techniques were similar to those used in a later study of boron penetration from colemanite (10), except that it was necessary to use an auger in the stiff clay below the 12-inch depth. Because the Arredondo soil was diluted by the pebbles throughout the profile, analytical calculations were based on an acre 7-inches for 2,000,000 pounds, whereas in the Lakeland, calculations were based on the conventional acre 6-inches for that weight of soil.

On the Lakeland soil, borax was applied to well-established plots of centipede

grass (*Eremochloa ophiuroides* (Munro) Hack) at rates of 0, 100, 400, and 800 pounds per acre. The material was broadcast on November 15, 1945, and the centipede grass sod was allowed to remain undisturbed throughout the experiment. As with the Arredondo soil, samples were taken about 4, 12, and 24 months after the borax was applied. With this lighter, more permeable soil the 0-42-inch sampling depth was divided into only four zones: plow depth (0-6 inches) and each successive foot below. Since the grass was dormant at the time

TABLE 1

Boron in Arredondo loamy fine sand from surface-applied borax*

Rainfall: 4 months, 34.51 inches; 12 months, 59.65 inches; 24 months, 124.99 inches

BORAX APPLIED	DEPTH OF SAMPLE	NATIVE SOIL BORON	BORON FOUND† AFTER		
			4 Months	12 Months	24 Months
<i>lb./A.</i>	<i>in.</i>	<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>
100	0-3	0.22	0.55	0.41	0.21
	3-7	0.11	0.45	0.33	0.14
	7-14	0.04	0.40	0.47	0.18
	14-21	0.03	0.90	0.73	0.28
	21-28	0.06	0.98	0.86	0.33
	28-35	0.07	0.57	0.79	0.36
400	35-42	0.08	0.40	0.51	0.48
	0-3	0.22	0.65	0.37	0.26
	3-7	0.11	0.62	0.36	0.19
	7-14	0.04	1.25	0.42	0.14
	14-21	0.03	2.60	1.03	0.23
	21-28	0.06	2.38	1.75	0.42
1600	28-35	0.07	1.35	2.25	0.69
	35-42	0.08	0.83	2.00	1.03
	0-3	0.22	1.15	0.98	0.50
	3-7	0.11	0.98	0.66	0.29
	7-14	0.04	2.00	1.05	0.38
	14-21	0.03	7.20	4.60	1.32
	21-28	0.06	10.80	10.60	2.77
	28-35	0.07	13.00	14.00	4.27
	35-42	0.08	9.00	11.40	5.40

* Boiling-water extractable from air-dried soil.

† All values include the native soil boron, which was found to vary with seasonal conditions. Therefore, specific values for the successive sampling periods were used in arriving at net retention for the determinations in table 2; but, for simplicity, only the means are shown here (see column 3).

of borax application, no toxicity was evident. By spring, when growth began again, there appeared to be little or no adverse effect upon the grass or volunteer weeds, even from the 800-pound rate. The soil samples were analyzed within about 2 to 12 months from the time they were obtained in the field, the mean elapsed time being approximately 6 months.

RESULTS

Table 1 shows that after 4 months the maximum concentration of boron in the Arredondo soil was found at about the 28-inch depth. Notable amounts

were found to have penetrated as far as the 35-42-inch zone and some boron may have leached below the 42-inch depth. A maximum of 59.3 per cent was recovered as boiling-water-extractable boron in the 0-42-inch zone (table 2). What fixation of boron there was in this soil appears to have taken place during the first 4 months, as the total percentage recovered was only slightly less at

TABLE 2
Boron retained in Arredondo loamy fine sand from surface-applied borax

BORAX APPLIED	DEPTH OF SAMPLE	BORON RETAINED* AFTER		
		4 Months	12 Months	24 Months
<i>lb./A.</i>	<i>in.</i>	%	%	%
100	0-3	2.9	1.4	0.0
	3-7	3.8	1.9	0.4
	7-14	6.4	7.4	2.5
	14-21	15.7	11.5	4.2
	21-28	16.4	13.8	5.1
	28-35	8.6	12.5	5.3
	35-42	5.5	7.2	7.4
Total		59.3	55.7	24.9
400	0-3	0.9	0.3	0.1
	3-7	1.4	0.6	0.2
	7-14	5.3	1.6	0.4
	14-21	11.4	4.2	0.8
	21-28	10.3	7.4	1.7
	28-35	5.6	9.6	2.8
	35-42	3.3	8.4	4.3
Total		38.2	32.1	10.3
1600	0-3	0.5	0.4	0.1
	3-7	0.6	0.3	0.1
	7-14	2.2	1.1	0.4
	14-21	7.9	5.0	1.4
	21-28	11.8	11.6	3.0
	28-35	14.2	15.3	4.6
	35-42	9.8	12.5	5.9
Total		47.0	46.2	15.5

* As boiling-water extractable.

12 months than at 4 months. The drop from 59.3 to 55.7 per cent for the 100-pound rate is believed to represent only the amount of boron which had moved below the 42-inch depth in the intervening 8 months. The clay subsoil, therefore, had the ability to retard downward progression to a marked degree but apparently had no capacity for progressive fixation. This is borne out also by values for the higher applications, especially for the 1,600-pound rate, which

decreased only from 47.0 to 46.2 per cent. As there was prolonged retention of boron at about the 28-35-inch depth, the maximum concentration was not found in the 35-42-inch depth until 24 months after application.

The 4-month samples of topsoil and upper subsoil for all locations showed that the percentage of boron retained was inversely related to the amount of borax applied (table 2). The explanation appears to be that the high applications of boron departed farther and farther from the very small amount which this soil is capable of holding in stable equilibrium. Though these percentages offered a means for studying the rate of disappearance for the various borax levels, residual toxicity should be evaluated on the basis of actual amounts, as pounds

TABLE 3

Boron in Lakeland fine sand from surface-applied borax*

Rainfall: 4 months, 16.56 inches; 12 months, 64.35 inches; 24 months, 128.45 inches

BORAX APPLIED	DEPTH OF SAMPLE	NATIVE SOIL BORON	BORON FOUND† AFTER		
			4 Months	12 Months	24 Months
<i>lb./A.</i>	<i>in.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
100	0-6	0.08	0.29	0.14	0.08
	6-18	0.04	0.19	0.09	0.04
	18-30	0.03	0.11	0.08	0.02
	30-42	0.03	0.09	0.06	0.01
400	0-6	0.08	1.05	0.20	0.14
	6-18	0.04	0.58	0.09	0.06
	18-30	0.03	0.33	0.08	0.04
	30-42	0.03	0.23	0.06	0.04
800	0-6	0.08	1.65	0.29	0.18
	6-18	0.04	0.97	0.27	0.11
	18-30	0.03	1.03	0.18	0.09
	30-42	0.03	0.58	0.16	0.09

* Boiling-water extractable from air-dried soil.

† The net retention of boron from borax, for calculating percentage boron retained in table 4, was obtained by subtracting the mean values for native soil boron shown in column 3.

of borax per acre. The amounts remaining in the 0-7-inch depth from the 100-, 400-, and 1,600-pound applications were, respectively, 6.7, 9.2, and 17.6 pounds of borax per acre after 4 months; 3.3, 3.6, and 11.2 pounds after 12 months; and 0.4, 1.2, and 3.2 pounds after 24 months. Since the average application of borax as a plant nutrient is at the rate of about 10 pounds per acre, the only value which might prove notably toxic even to boron-sensitive plants was 17.6 pounds, residual from the 1,600-pound rate 4 months after application.

In the Lakeland soil, although the rainfall for the first 4 months was only 16.56 inches compared with 34.51 inches for Arredondo, boron was lost from the profile at a much faster rate (see tables 3 and 4). In the 0-42-inch zone Arredondo retained 59.3 per cent of the 100-pound application while Lakeland retained only 13.9 per cent. Plow depth retention by Lakeland 4 months after

application of 100, 400, and 800 pounds of borax per acre was 3.7, 4.3, and 3.5 per cent, respectively. Failure to develop the inverse relationship noted for Arredondo between borax applied and percentage boron retained may have been because Lakeland was under an established sod and rainfall was limited. In spite of these retarding factors, leaching in Lakeland fine sand was so rapid that concentration maxima were not observed, apparently because they had passed below the 42-inch depth before the 4-month samples were taken. The amounts remaining in the topsoil from the 100-, 400-, and 800-pound applications were, respectively, 3.7, 17.2, and 28.0 pounds of borax per acre after 4

TABLE 4
Boron retained in Lakeland fine sand from surface-applied borax

BORAX APPLIED	DEPTH OF SAMPLE	BORON RETAINED* AFTER		
		4 Months	12 Months	24 Months
<i>lb./A.</i>	<i>in.</i>	%	%	%
100	0-6	3.7	1.1	0.0
	6-18	5.3	1.8	0.0
	18-30	2.8	1.8	0.0
	30-42	2.1	1.1	0.0
Total		13.9	5.8	0.0
400	0-6	4.3	0.5	0.3
	6-18	4.8	0.4	0.2
	18-30	2.6	0.4	0.1
	30-42	1.8	0.3	0.1
Total		13.5	1.6	0.7
800	0-6	3.5	0.5	0.2
	6-18	4.1	1.0	0.3
	18-30	4.4	0.7	0.3
	30-42	2.4	0.6	0.3
Total		14.4	2.8	1.1

* As boiling-water extractable.

months; 1.1, 2.0, and 4.0 pounds after 12 months; and 0.0, 1.2, and 1.6 pounds after 24 months. Though the 17.2- and 28.0-pound residuals in this light sandy soil should be rated as toxic to plants, borax in what might be considered herbicidal quantities did not remain in the topsoil of either the Lakeland or the Arredondo soil for as long as 4 months from time of application, even from the highest rates of 800 and 1,600 pounds per acre.

DISCUSSION

Any interpretation of borax residuals should take into account whether the effects upon plants might be toxic or herbicidal. This is a matter of degree, as

the former would be injurious only, while the latter would be lethal. Toxic effects with certain plants on light sandy soils sometimes are observed in the range of 10 to 15 pounds of borax per acre. These effects usually are temporary, after which the plants are likely to recover. But for borax to have lethal or herbicidal effects over a wide range of plants it usually would have to be present in quantities of several hundred pounds per acre.

The data in this study indicate that for well-drained sands under high annual rainfall the elimination of residual toxic effects from heavy applications of borax may not constitute a serious problem where the soil is not to be used for economic crops less than 1 year from time of treatment. It would seem, however, that borax as a herbicide might prove ineffectual under these conditions because it is leached so rapidly from the topsoil and upper subsoil. For herbicidal use in humid climates the less soluble calcium borate, colemanite (9), seems a more appropriate source. This mineral in 20-40-mesh size at low rates per acre is an excellent source of boron for plant nutrition, but preliminary observations where applied at the rate of about 225 pounds per acre (10) indicate that when finely ground it may be a more effective herbicide than borax. On Rex fine sand at this rate it gave much greater temporary retention in the topsoil and was much more toxic to plants, yet over a period of 12 months it leached from topsoil and subsoil as completely as did borax.

SUMMARY

Borax was applied to Arredondo loamy fine sand at rates of 0, 100, 400, and 1,600 pounds per acre and to Lakeland fine sand at rates of 0, 100, 400, and 800 pounds per acre. The former received during the 4-, 12-, and 24-month periods of the experiment a rainfall of 34.51, 59.65, and 124.99 inches, respectively; the latter, a deep sand, received during corresponding periods a rainfall of 16.56, 64.35, and 128.45 inches. Reaction was about pH 5.6 in both soils.

Analysis for boiling-water-extractable boron at 4 months showed notable penetration into the clay subsoil of Arredondo, with the maximum concentration from the 100-pound rate at the 21-28-inch depth, while from 1,600 pounds the maximum was at the 28-35-inch depth. Maximum concentration was not found in the 35-42-inch depth until 24 months after application. For Lakeland no concentration maxima were observed, as these apparently had passed below the 42-inch depth before the 4-month samples were taken.

Amounts remaining in the 0-7-inch depth of Arredondo from applications of 100, 400, and 1,600 pounds were, respectively, 6.7, 9.2, and 17.6 pounds of borax per acre after 4 months; 3.3, 3.6, and 11.2 pounds after 12 months; and 0.4, 1.2, and 3.2 pounds after 24 months. In Lakeland the amounts remaining in the topsoil from the 100-, 400-, and 800-pound applications were, respectively, 3.7, 17.2, and 28.0 pounds of borax per acre after 4 months; 1.1, 2.0, and 4.0 pounds after 12 months; and 0.0, 1.2, and 1.6 pounds after 24 months.

Borax in herbicidal quantities did not remain in the topsoil of either Lakeland fine sand or Arredondo loamy fine sand for as long as 4 months from time of application, even from amounts as high as 800 and 1,600 pounds per acre.

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FIELD TEST FOR ACTIVE SULFIDES IN SOIL

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Received for publication January 28, 1952

Increasing land areas of several midwestern states are being subjected to the devastation of strip-mining. The revegetation of this strip-mine waste land is of considerable importance in the rebuilding and conservation of natural resources. In such a program, preliminary tests of the soil are desirable to detect limiting factors of plant growth and reproduction and to determine the best type of plantings to be recommended, as for successful reforestation. Such a study is one of the projects of the Central States Forest Experiment Station of the U. S. Department of Agriculture, and discussions initiated by members of the staff of the local station led to a field test that appears useful in their program for the rehabilitation of these waste lands.

Ecological studies by Croxton (2) have shown that strip-mine wastes containing large amounts of sulfur compounds, particularly iron pyrites, have a restricted capacity for revegetation, probably because of development of undesirable acid conditions. He found in the spoil banks a pH range from 2.6 to 9.0, with vegetation surviving only above pH 4.5 and becoming established at about pH 5. The greatest acidity developed from exposed pyrites, which occurred in the shale layer. The reaction $2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$, as well as bacterial action, was suggested by Li and Parr (5) for the production of most of the acid conditions found in the overburden exposed to air and moisture.

Extensive work has been done on the determination of sulfur and sulfur compounds in soils, coal, coke, slag, and minerals. Several agencies have evaluated the various procedures and have recommended the methods of Eschka, Lunge, Parr, and others (3, 4, 6, 7, 8). All of these methods, however, require laboratory procedures that are involved and time-consuming. Of immediate concern to the local station was a simple field test for sulfides and pyrites that could be used by survey parties to predict probable future soil acidity. Of the several methods tried, the following procedure was found most acceptable.

PROCEDURE

Put 2-3 gm. of the material to be tested into a 20- by 150-mm. test tube and mix with about 1 gm. of granular c. p. zinc (20-30-mesh). Insert a spiral of copper wire halfway down the tube to disperse bubbles that otherwise might rise to the top and spoil the test by contact with the test paper. Add 2-3 ml.

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The authors are indebted to G. H. Deitschman, of the Central States Forest Experiment Station, Carbondale Branch, for directing the collection and testing of field samples. The areas surveyed and the various levels of overburden used as a source of the samples will be discussed in a bulletin of that station.

(one eyedropperful) of 6 N HCl. Wait about 5 seconds for the fumes to displace the air in the test tube, and then place over the mouth of the tube a small filter paper circle impregnated with lead acetate. Remove the filter paper after 5 seconds. The color and general appearance of the deposit produced on the

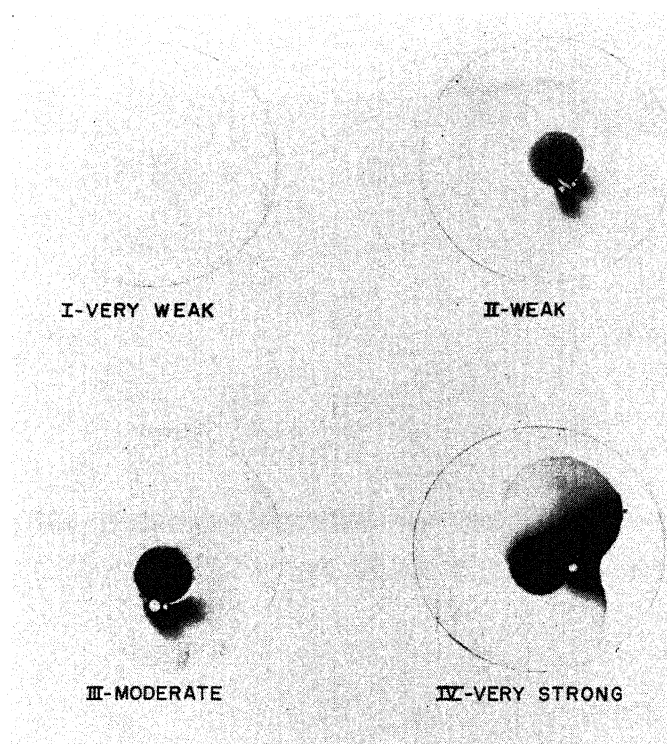


Fig. 1. Results of Field Tests for Active Sulfides

I, slight tan discoloration; II, tan; III, brown with tan edge; IV, black with silvery cast.

filter paper (fig. 1) are indicative of the quantity of potentially active sulfide or pyrites in the sample, as follows:

Slight tan coloration.....	Very weak
Tan.....	Weak
Brown with tan edge.....	Moderate
Block with silvery cast.....	Very strong

This test has been used at numerous strip mines in Illinois and Indiana by personnel of the Experiment Station. No claim for originality is made for the method, as it involves well-known chemical reactions. But the test kit requires only test tubes, test papers, dilute HCl, zinc, and a rock hammer.

The tests were applied to portions of the excavated shale (and occasionally sandstone) that in most cases occurs immediately above the coal vein that is to

be mined. According to Croxton (2), shale is the major contributor of potential acidity in the spoil banks. Limestone seems to occur seldom in such rock, but if it is present, the CO_2 evolved in the test probably would not vitiate the lead acetate test for the available sulfide and pyrites.

LABORATORY VERIFICATION

A question almost immediately arose: Is there any correlation between the field tests and total sulfur? To determine this, the samples of shale from strip-mine overburden that were used in field tests were analyzed for total sulfur by the Eschka method (1, pp. 77-79).

TABLE 1
Analyses for sulfur in field-tested samples of shale

SAMPLE	FIELD TEST	SAMPLE WEIGHT	BaSO ₄ OBTAINED	SULFUR
		gm.	gm.	%
I	Very weak	0.6963	0.0030	0.061
		0.6882	0.0030	0.060
		0.6871	0.0032	0.064
II	Weak	1.0095	0.0065	0.088
		0.6966	0.0055	0.108
		0.6976	0.0064	0.126
III	Moderate	0.9576	0.0145	0.208
		0.9112	0.0151	0.228
		1.2350	0.0200	0.222
IV	Very strong	0.6065	0.0988	2.24
		0.5036	0.0870	2.37
		0.4602	0.8000	2.39

Briefly, the sample was ground to 100-mesh fineness, and approximately 1 gm. was mixed well with 3 gm. of the Eschka mixture (2 parts MgO + 1 part Na_2CO_3). This mixture was placed in a platinum crucible, then in a cold electric muffle furnace. The temperature was raised to 800°C ., at which the mixture was ignited for 2 hours. After cooling, the ignited product was leached with hot distilled water. The resulting solution, after treatment with bromine to ensure oxidation of all the sulfur to the sulfate state, was used for the usual BaSO_4 gravimetric determination. From this the percentage of total sulfur in the shale was calculated (table 1). Both Munktells No. OK filter paper and fine porcelain filtering crucibles (Selas No. 2001) were used with little variance in results.

CONCLUSION

The results of the laboratory analyses seem to indicate that there is a general correlation between the total sulfur and the described lead acetate field test as applied to shales found in coal strip-mine wastes. The variation between duplicate samples is rather large, probably because of improper sampling; nevertheless, the distinction between samples, previously labeled "very weak" to "very strong" in the field tests, is significant.

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INFLUENCE OF SOIL AGGREGATION ON PLANT GROWTH

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Received for publication February 29, 1952

Soil structure is defined as the arrangement of soil particles (3, pp. 124-192). At present no method is available for direct evaluation of soil structure thus defined, though the problem has been reviewed by a number of workers (1, 5, 19, 20, 21, 22). Many researchers (7, 9, 10, 11, 14, 15, 28, 29, 30) use the analysis of size and water stability of aggregates as an indicator for soil structure. In Israel, Ravikovits and Hagin² used the aggregate analysis as a measure of structure. The influence of structure, in general, on crop yields has been investigated by a number of workers (4, 6, 12, 13, 16, 23).

The present work was undertaken further to elucidate the relations found in the aforementioned papers. In particular, it was desired to investigate the relation between plant growth and soil structure as found by aggregate analysis. For this purpose, plants were grown in greenhouse pots, the only known independent variant in the different soils being the size of aggregates.

EXPERIMENTAL PROCEDURE AND RESULTS

Mechanical analysis of soil was made by Beam's Sudan method. Carbonates were determined with an apparatus similar to Scheibler's (31). Organic matter was found by Tiurin's wet oxidation method. Water-soluble nitrates and phosphorus were determined on 10:1 water extracts of soil by the phenoldisulfonic acid method (31) and the Truog method (25), respectively. Available phosphorus was evaluated as described by Truog. Total porosity was calculated from the real specific gravity (26) and from the apparent density, which was evaluated from direct measurements of the volume and weight of soil in pots. The non-capillary porosity was calculated from the pore space and "field capacity" of the soil in pots. The field capacities for all treatments were found by wetting by top irrigation, to two thirds of their depth, soil columns which were approximately the depth of a pot, and determining their moisture content at various heights after 2 days. The uppermost layer was rejected, and the mean moisture content of the approximately uniform moist upper layers was used for expressing the field capacity.

The soil for the experiment was taken from the lands of the settlement Eilon, in the western Galilee hills. It is red heavy clay, typical of the soils in the mountainous regions of Israel. Some of its characteristics are listed in table 1.

¹ The author wishes to express his thanks to S. Ravikovits for enabling him to perform this work and to J. Rubin for his many helpful suggestions. The author is also indebted to G. B. Bodman for his interest in the preparation of the manuscript.

² Ravikovits, S., and Hagin, J. Structure of some typical Israeli soils. (Not yet published.)

Three grades of aggregate size were prepared by the following treatments:

Treatment C, coarse aggregates. The natural clods were broken by hand. It was assumed that the aggregates remained in their natural size.

Treatment M, medium-sized aggregates. The clods were broken in a porcelain mortar until they passed through a 2-mm. screen.

Treatment F, fine aggregates. The soil was ground in a mill until it passed through a 0.5-mm. screen.

TABLE 1
Analysis of Eilon soil before treatment

MECHANICAL ANALYSIS				CaCO ₃	ORGANIC MATTER	pH
Coarse sand 2-0.2 mm.	Fine sand 0.2-0.02 mm.	Silt 20-2 μ	Clay <2 μ			
%	%	%	%	%	%	
1.0	20.9	17.6	60.5	0	4.30	7.09

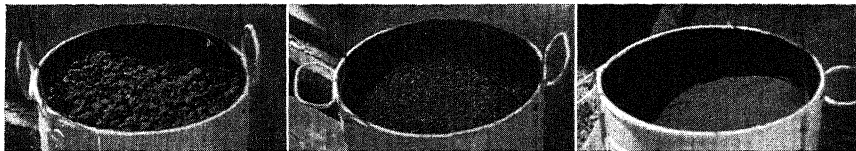


FIG. 1. Appearance of Soils Before Planting

Left to right: treatment C, coarsely aggregated soil; treatment M, soil of medium aggregation; treatment F, finely aggregated soil.

TABLE 2
Analysis of soils before planting
Oven-dry basis

TREATMENT*	MECHANICAL ANALYSIS				REAL SPECIFIC GRAVITY	FIELD CAPACITY	PORE SPACE	NONCAPILLARY POROSITY	ORGANIC MATTER	WATER-SOLUBLE		AVAILABLE P
	Coarse sand	Fine sand	Silt	Clay						NO ₃	P	
	%	%	%	%		%	%	%	%	ppm.	ppm.	ppm.
C	0.8	21.5	17.6	60.1	2.36	30	61.6 \pm 0.3	34.4 \pm 0.4	4.22	24	0.16	16.8
M	1.0	20.9	17.6	60.5	2.36	38	59.2 \pm 0.5	22.2 \pm 1.2	4.30	24	0.16	16.8
F	0.7	21.5	17.6	60.2	2.36	39	56.3 \pm 0.9	15.9 \pm 1.8	4.93	24	0.16	16.8

* C = coarse aggregates, clods broken by hand; M = medium-sized aggregates, clods broken in mortar to pass through a 2-mm. screen; F = fine aggregates, soil ground in mill to pass through a 0.5-mm. screen.

Metal pots, on the bottom of each of which was placed a layer of shells, were filled with 7-kgm. lots of air-dry soils prepared by the three treatments (fig. 1), each treatment being replicated five times.

Some characteristics of the soils in the pots are given in table 2. The table shows that many of the properties measured changed but little in the course of treatment. The percentage of organic matter increased in the finer aggregates; presumably, part of the plant residues that were ground during the treatment

were oxidized by the analytical method used. The volumes of noncapillary porosity show marked differences. The difference between the coarsely aggregated soils and those of medium aggregation is highly significant (1 per cent level of significance), and that between the medium and finely aggregated samples is very significant (2 per cent level).

Before planting, analyses of aggregates were performed on representative soil samples. The method used was essentially Yoder's (32). Three sieving procedures were followed: 1. dry sieving; 2. wet sieving, the air-dry aggregates being wet by capillarity before being sieved; 3. wet sieving, the air-dry aggregates being immersed suddenly in water before being sieved. To express the results of these analyses in one number, mean weight-diameters were calculated as suggested by Van Bavel (2).

TABLE 3
Aggregate analysis of soils before planting

SIZE OF AGGREGATES	TREATMENT C—PROCEDURE*			TREATMENT M—PROCEDURE			TREATMENT F—PROCEDURE		
	1	2	3	1	2	3	1	2	3
mm.	%	%	%	%	%	%	%	%	%
>1	99.6	91.8	95.4	46.2	52.6	33.4	6.6	9.1	7.8
1-0.5	0.4	3.0	1.7	22.8	20.3	28.7	8.0	14.7	11.6
0.5-0.25	—	2.9	1.9	18.4	12.2	17.3	35.6	33.1	29.7
0.25-0.15	—			2.8	2.5	3.7	8.6	7.7	8.2
0.15-0.07	—			6.8	3.7	5.1	24.2	13.5	14.3
<0.07	—	2.3	1.0	3.0	8.7	11.8	17.0	21.8	28.7
Mean weight-diameter	1.70	1.54	1.59	1.00	0.95	0.81	0.33	0.39	0.34

* See footnote table 1 for treatments. Procedures: 1, dry sieving; 2, wet sieving—air-dry aggregates wet by capillarity; 3 wet sieving—air-dry aggregates immersed suddenly in water.

Table 3 demonstrates the well-known fact that results of aggregate analysis are influenced by the method used. Nevertheless, all procedures yielded similar and significant differences in aggregation among the three soils.

In addition to the physical and aggregate analyses, permeabilities of water-saturated samples were measured by a method described by Graecen³. Only the medium and the finely aggregated soils were tested, because of lack of suitable apparatus for the coarsely aggregated one. These tests provided additional evidence (fig. 2) that considerable structural differences existed between the two samples tested.

The pots were sown on December 25, 1950, with a local variety (Nursit) of *Triticum durum* and were kept in a greenhouse. No fertilizers were added. The pots were watered to full field capacity, and the soil was kept approximately at this moisture content throughout the experiment. At first, water was added

³ Graecen, E. L. Applicability of Boyd's exchange equations to cation exchange in soil columns. 1949. [Unpublished doctor's thesis, Univ. Calif.]

every 2 days; later, every day. In every pot, 10 plants were grown. On April 2, 1951, the plants were harvested and the green parts were measured, weighed, and analyzed (18).

At the time of harvest, 90 per cent of the plants in treatment C, about 40 per cent in treatment M, and none in treatment F were in bloom.

The differences in yields from the various treatments are highly significant (1 per cent level). As is obvious from table 4, the smaller plants absorbed more nitrogen and less phosphorus and potassium per unit weight than did the larger

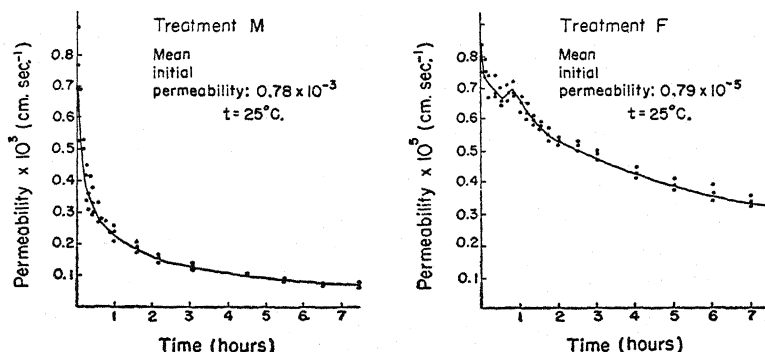


FIG. 2. Permeabilities of Water-Saturated Samples of Medium Aggregated (M) and Finely Aggregated (F) Soils

TABLE 4
Yields and composition of wheat plants grown in soils
Mean per pot

SOIL TREAT- MENT*	HEIGHT OF PLANTS	FRESH WEIGHT OF PLANTS	DRY WEIGHT OF PLANTS	COMPOSITION OF PLANTS†					
				N		P		K	
	cm.	gm.	gm.	%	gm.	%	gm.	%	gm.
C	90.5 ± 1.7	78.6 ± 2.0	20.1 ± 0.7	0.89	.179	.113	.023	1.98	.398
M	83.8 ± 1.6	64.3 ± 2.8	16.5 ± 0.9	0.93	.154	.067	.011	1.46	.241
F	41.3 ± 3.0	31.8 ± 3.1	5.8 ± 0.7	1.51	.088	.064	.004	1.43	.083

* See footnote table 1.

† Oven-dry basis.

ones. The total absorption of nutrient elements from the pots was always greatest, however, in the more fully developed plants.

Immediately after the plants were harvested, soil samples from the pots were analyzed to determine the changes in nutrient status (table 5) and aggregation (table 6). In making the aggregate analyses, besides wet-sieving procedure 3 previously followed, in which soil samples from the pots were air-dried and then immersed suddenly in water and analyzed, wet samples as they came from the pots were given the immersion and sieving treatment (procedure 3a).

Comparison of table 5 with table 2 shows that virtually no changes occurred in the nitrate content of the soils during plant growth. Water-soluble phos-

phorus increased in two of the three treatments. On the other hand, the amount of available phosphorus was lowered in all treatments, from 16.8 ppm. at the beginning of the experiment to approximately 2 ppm. at the end.

The results of the aggregate analyses (table 6), when compared with those in table 3, show that during plant growth there were only slight changes in the coarsely aggregated soil and that of medium aggregation. In the finely aggregated soil, however, the trend to form coarser aggregates is evident. It seems

TABLE 5
Analysis of soil after harvest
Oven-dry basis

TREATMENT*	WATER-SOLUBLE		AVAILABLE P	ORGANIC MATTER
	NO ₃	P		
	ppm.	ppm.	ppm.	%
C	20.0	0.32	2.4	4.98
M	18.2	0.16	2.2	4.46
F	23.5	0.27	2.2	4.62

* See footnote table 1.

TABLE 6
Aggregate analysis of soil samples after harvest

SIZE OF AGGREGATES	TREATMENT C—PROCEDURE*		TREATMENT M—PROCEDURE		TREATMENT F—PROCEDURE	
	3a	3	3a	3	3a	3
mm.	%	%	%	%	%	%
>1	62.5	89.4	41.7	45.1	16.5	39.6
1-0.5	12.7	6.1	16.6	24.7	12.9	16.1
0.5-0.25	5.6	2.9	12.1	16.4	24.7	23.8
0.25-0.15	1.3	1.5	4.7	4.3	6.2	6.5
0.15-0.07	3.7	—	4.1	5.8	10.0	8.8
<0.07	14.2	0.1	20.8	3.7	29.7	5.2
Mean weight-diameter	1.11	1.53	0.82	0.94	0.47	0.83

* See footnote table 1 for treatment. Procedure 3 is the same as that in table 3; procedure 3a is similar to procedure 3 except that samples were not dried before immersion.

from table 6 that air-drying improved aggregation, and this is especially noticeable in the finely aggregated soils.

To obtain some indication as to why the more finely aggregated soil samples produced significantly lower yields than the coarsely aggregated soils, an additional experiment was performed.

The three soils were incubated for 24 days at 27°C. with free access to air. The packing and watering conditions were the same as for the soils in the pots, but no plants were grown. The samples were analyzed for water-soluble nitrates

and phosphates and for available phosphates. The results are presented in table 7. Since no chemical differences were found in the soils before incubation (table 5), it seems that incubation produced considerable differences in water-soluble nitrates and P in the various soils. The more finely aggregated soils contained definitely smaller quantities after incubation.

TABLE 7
Analysis of soils after 24 days of incubation at 27°C.

TREATMENT*	WATER-SOLUBLE		AVAILABLE P
	NO ₃	P	
	<i>ppm.</i>	<i>ppm.</i>	<i>ppm.</i>
C	62	0.47	11
M	38	0.38	9
F	12	0.12	7

* See footnote table 1.

DISCUSSION AND CONCLUSIONS

From the results reported, it may be concluded that, under the experimental conditions studied, coarsely aggregated soils produced better plant growth than did finely aggregated soils. Some preliminary conclusions may be drawn as to the reasons for this phenomenon.

The total soil porosity was not changed by variations in aggregate size. The ratio between capillary and noncapillary porosity, however, was influenced by the treatments. Differences in the pore size distribution are also indicated by considerable variations in permeability. Because of these facts and because of the irrigation procedure used, the air volume in the more finely aggregated soils was smaller than that in the coarsely aggregated soils. The probable result was poorer supply of oxygen to the roots and microorganisms living in the finely aggregated soils.

If this assumption is true, at least two causes for the depression of plant growth are possible: First, roots that suffer from lack of oxygen have a reduced ability to absorb nutrient elements. This has been reported by Hoagland (8), Bayer (5), Lawton (12), and others. Second, the quantities of available nutrients in the soil may be depressed. As no fertilizers were added, the plants were dependent on the naturally occurring nutrient reserves and on a steady supply of available nutrients released from nonavailable forms. Some of the latter possibly originate from decomposition of soil organic matter (27). The experimental results in table 7 seem to indicate that this decomposition was depressed in the more finely aggregated soil samples, possibly because of poor air conditions. As is evident from table 5, however, the quantities of nitrates were virtually equal in the three treatments after harvest. A possible explanation is that in the coarsely aggregated soil the supply as well as the consumption of nitrates was higher than in the finely aggregated soil.

Another indication of nutrient deficiency is provided by the fact that the

plants growing in the finely aggregated soil showed symptoms of nitrogen and phosphorus deficiency.

As to absorption of nitrogen, table 4 shows that plants growing on the finely aggregated soil absorbed relatively more nitrogen than did those on the coarsely aggregated soil. Shive *et al.* (17, 24), who grew plants in nutrient solutions with a poor oxygen supply, obtained similar results. These authors suggested that in oxygen-deficient substrate the plants obtained the needed oxygen from nitrates, and hence, the relatively great absorption of nitrogen by such plants. The similarity between these experiments and ours again suggests that the plants grown in the finely aggregated soil suffered from lack of oxygen.

One more conclusion may be drawn from the experiments; namely, that great care must be taken in performing certain types of pot experiments for fertilizer tests, as considerable differences in yields may be induced by structural changes of the soils in pots.

SUMMARY

A greenhouse experiment was performed to investigate the relation between plant growth and soil structure as found by aggregate analysis.

Three forms of aggregate sizes were prepared by crushing the clods of a heavy, red clay soil that has naturally very coarse aggregates.

The crushing did not induce chemical or textural changes in the soil treated, so far as it was tested. The size of aggregates was the only independent variant.

Wheat was grown in greenhouse pots. The variously aggregated soils produced highly significant differences in yields. The coarsely aggregated soil produced much better plant growth than did the finely aggregated soil.

As a possible cause of the reduced yields in the finely aggregated soils, insufficient supply of oxygen is suggested. Presumably the low supply of oxygen influenced at least two processes: it diminished the ability of roots to absorb nutrients, and it depressed the supply of some available nutrients to the growing plants. Some evidence is given in support of this suggestion.

It is noted that structural changes of the soil may considerably influence results of fertilizer tests.

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A DITHIZONE TISSUE TEST FOR ZINC IN PLANTS

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Received for publication March 15, 1952

In testing soils for zinc with dithizone,² it is observed occasionally that small particles of organic matter turn red. This behavior suggested that dithizone reacts with zinc in the plant residues. Investigation of this hypothesis resulted in the development of a simple tissue test for zinc in plants. Such a test might be useful in comparing the zinc contents of different plant parts and plants grown under various conditions. This report on the test is made to supply information to others who may wish to correlate test results with field observations.

The proposed test is as follows: Slice the plant tissue with a sharp knife and add a few drops of 0.01 per cent zinc-free dithizone in CCl_4 to the cut surfaces. Allow the CCl_4 to evaporate, protecting the test area from direct sunlight, which tends to fade the color of the zinc complex. The presence of zinc is shown by the formation of a red zinc dithizonate. Plants vary as to the amounts of zinc concentrated in different tissues, and the test must be interpreted accordingly.

It would be difficult to prove by direct means that a red stain produced by dithizone on plant tissue specifically indicates the presence of zinc. The amounts of the element causing the stain are very small, at most a few micrograms contained in the reacting surface of the tissue being tested. The pH conditions are more or less unknown except that they are neutral or slightly acid. The presence and amount of interfering elements are likewise uncertain. Furthermore, color intensity can be only qualitatively measured visually.

Several lines of evidence, however, offer proof that the proposed method is a test for zinc: (a) Zinc occurs in much higher concentration in plants than do any of the other elements which form reddish dithizonates; namely, bismuth, cadmium, cobalt, copper, indium, lead, mercury, palladium, silver, thallium, and tin.³ Ferrous iron, which is reported to form a red dithizonate at pH 6-7, does not produce a red color or interfere when FeSO_4 is applied to plant tissue at the time of the test application of dithizone. (b) Cut sections of fresh wheat plants when put in a separatory funnel containing ammonium acetate buffer at pH 7, dithizone in CCl_4 , and carbamate reagent, develop a red color at the nodes and spikelets, the same regions that are stained when dithizone is applied directly to the plants. Under these conditions, only the occurrence of abnormally high amounts of cadmium could interfere. Apparently no element normally occurring in plants interferes, and only zinc causes the color reaction which occurs in the tissue. (c) An experiment was performed which further establishes

¹ This investigation was supported in part by the U. S. Atomic Energy Commission.

² Shaw, E., and Dean, L. A. Use of dithizone as an extractant to estimate the zinc nutrient status of soils. *Soil Sci.* 73: 341-347, 1952.

³ Sandell, E. B. *Colorimetric Determination of Traces of Metals*, ed. 2. Interscience Publishers, Inc., New York. 1950.

a correlation between the accumulation of zinc in plants and the red staining by dithizone. Corn was grown in soil fertilized with 8 ppm. zinc having a specific activity of 20 mc. of radioactivity per gram. When the plants were mature, cuts were made through different parts of the plants and the tissue test was made with dithizone. A pronounced red stain was observed in the node tissue, indicating a high concentration of zinc. Likewise, a Geiger counter indicated a high concentration of radio zinc at the node locations and almost none at other parts of the plant.

More precise data were obtained in the following manner: Starting at 2 cm. above a central node of the corn plant, twenty-one 2-mm. sections were removed consecutively down the stalk with a rotary-blade meat-slicing machine. These sections were then treated with a few drops of dithizone reagent, which was allowed to evaporate. The top five sections (numbers 1 to 5) showed virtually no red color (or zinc). With decreasing distance from the node, there was a

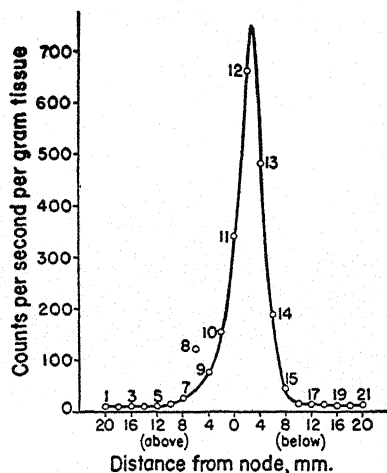


FIG. 1. Distribution of Radio Zinc About Node of Cornstalk

gradual increase in color, which reached maximum intensity in sections 11, 12, and 13. Sections 15 to 21 showed almost none. These same sections were then placed under a Geiger counter and the relative radio zinc content was quantitatively determined. The results are shown in figure 1.

These data illustrate the different relative concentrations of zinc within normal healthy plants. Within the short distance of 1 cm. along the stalk, zinc concentration increases 75-fold as the node is approached. Sections 1 to 7 and 15 to 21, as indicated by radioactivity tests, contain small amounts of zinc, whereas sections 11, 12, and 13 contain large amounts. The results from this proposed dithizone test and radioactivity measurements are very similar.

The proposed dithizone tissue test, accepted on the basis of the three lines of evidence presented, may offer a rapid method of assessing the relative zinc content of plants and variations of concentration within different parts of the same plants.

BOOKS

Fertilizers—A World Report on Production and Consumption. By Food and Agricultural Organization of the United Nations. Washington, D. C., 1952. Pp. 46. Price, paper-bound, \$0.25.

The authors of this report give data on production and consumption of fertilizers for the years 1950-51 and 1951-52, and estimates for 1952-53. World production and consumption, international trade, and general outlook are presented, as well as summaries of the fertilizer position of Europe, North and Central America, Africa, Asia, Oceania, and South America, from data supplied by the several governmental agencies up to July 20, 1952.

An Introduction to the Principles of Plant Physiology. Revised Edition. By WALTER STILES. Pitman Publishing Corporation, New York, 1950. Pp. 701, figs. 64. Price \$12.50.

The answer to almost any question one might raise in plant physiology can be found in this well-organized and well-developed volume. If the answer is not as yet known, the nearest approach is suggested. The original edition appeared in 1935, so it was necessary to do a considerable amount of revising to bring the book up to date. This applies particularly to enzymes, hormones, nitrogen metabolism, and mineral nutrition. The main divisions of the book are general physiology of the plant cell, metabolism, physiology of development, and irritability and movement. Some 1,200 important references and a well-developed index are appended. Every soil-plant scientist will find much of interest and value in this volume. Plant physiologists, in particular, will want a copy close at hand.

Introductory Mycology. By CONSTANTINE JOHN ALEXOPOULOS. John Wiley and Sons, Inc., New York, 1952. Pp. 482, figs. 186. Price \$7.

The name of the author adds to the interest of this book, as does that of the artist, Mrs. Sun Huang Sung, who is responsible for an excellent set of drawings illustrating the various species of fungi and closely related forms of plant life. One chapter is devoted to bacteria and actinomycetes, another to algal fungi, and a final short chapter to lichens. The purpose of the author is that of developing a good textbook for the beginning student of this subject, and he has succeeded in doing just that. The illustrations are of special interest in this connection. At the end of each chapter is a long list of references. The appendix contains an excellent glossary of mycological terms and acknowledgment of the sources of a large number of the references. The material is attractively presented and, in conjunction with laboratory exercises, should be of great interest to any student who is new to this field.

Paper Chromatography—A Laboratory Manual. By RICHARD J. BLOCK, RAYMOND LESTRANGE, AND GUNTER ZWEIG. Academic Press, Inc., New York, 1952. Pp. 195. Price \$4.50.

Much interest has developed in paper chromatography during the last 10 years. As a result, it is now possible to discuss the subject in some detail and to present some of the more modern techniques employed in this method of study. That is what the authors of this book have done. They first present the principles on which the technique is based and then develop the information on quantitative procedure with amino acids, carbohydrates, aliphatic acids, purines, phenols, antibiotics, vitamins, and related organic substances. The last chapter deals with inorganic separations, with special reference to trace elements of particular interest in plant and animal nutrition. Two illustrations in that chapter are diagrams related to separation of cations and an electrographic cell for continuous operation. A list of some 400 references is appended. The book fills an important need for those contemplating work in this field.

Plant Physiology. Second Edition. By BERNARD S. MEYER AND DONALD B. ANDERSON. D. Van Nostrand Company, Inc., New York, 1952. Pp. 784, figs. 183. Price \$8.50.

This is virtually a new book. Much of the content of the first edition has been rewritten and much new material has been added. The 36 chapters cover a wide range of topics in plant physiology, all with a high degree of clarity of expression. The discussions of colloidal systems, plant cells, soil-water relations, enzymes, photosynthesis, fat and nitrogen metabolism, translocation of solutes, hormones, and growth periodicity are of special interest. The illustrations are excellent. A long list of references and some very useful questions are appended to each chapter. Reference is made to the work of more than 1,000 research specialists, mostly in the field of plant physiology. The book should prove highly useful as a text for students who are well trained in physics and chemistry.

Seaweeds and Their Uses. By V. J. CHAPMAN. Pitman Publishing Company, New York, 1949. Pp. 287, figs. 52, plates 20. Price \$6.

Almost everyone would like to know more about the possible usefulness of seaweeds as food and feed, for manurial purposes, and as a source of important industrial chemicals. The author of this book has obliged by giving an excellent review of the literature on the subject. He discusses the various species, the points of supply, and the special values each may have. Maps of the most important seaweed beds are shown. Techniques for the collecting and processing of seaweed are discussed. Special uses, such as for agar-agar, medicinal products, and iodine, are considered in detail. It is of particular interest to note that seaweed, on a dry-weight basis, may contain as high as 4.04 per cent nitrogen, 3.78 per cent fat, 45.4 per cent ash, 0.43 per cent phosphorus, 31.6 per cent potash, and 0.32 per cent iodine. A bibliography of some 800 references is appended. The illustrations, notable the plates, are highly instructive. This is a very interesting book, by the reading of which one can see that important possibilities lie ahead in the more complete development of the seaweed industry.

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